Composition, Sources of PM$_{2.5}$ Saccharides and its characteristics during the haze episode in Shanghai

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Abstract: The characteristics of biogenic aerosols in urban area were explored by determining the composition, temporal distribution of saccharides in PM$_{2.5}$ in Shanghai. The total saccharides showed a wide range of 15.2 ng/m$^3$ to 1752.8 ng/m$^3$, with the averaged concentrations were 169.8 ng/m$^3$, 300.5 ng/m$^3$, 288.4 ng/m$^3$, 688 ng/m$^3$ in spring, summer, autumn, and winter, respectively. The concerned saccharides include anhydrosaccharides (levoglucosan and mannosan), which were higher in cold seasons due to the increased biomass burning, saccharide alcohols (mannitol, arabitol, sorbitol) and monosaccharides (fructose, glucose), which showed more abundant in warm seasons attributed to the biological emissions. By PMF analysis, four emission sources of saccharides were demonstrated, including biomass burning, fungal spores, soil suspension and plant pollens. Resolution of backward trajectory and fire points showed a process of high concentrations of levoglucosan. We found that concentrations of anhydrosaccharides showed relatively stable under different pollution levels while saccharide alcohols exhibited an obvious decrease, indicated that biomass burning was not the core reason of the heavy haze pollution, however, and high level PM$_{2.5}$ pollution might inhibit effects of biological activities.

Keywords: Saccharides; Biomass burning; Haze; Source apportionment; Bio-aerosol

1. Introduction

Organic aerosols are important parts of fine atmospheric particulate matter, which account for about 20%-60% of the PM$_{2.5}$ mass in urban sites, 30%-50% in remote areas, and even 90% in low troposphere [1]. The compositions of organic aerosols are very complex and diverse with variable characteristics, among which the water-soluble organic components (WSOC) are the most important species, and the percent of WSOC in organic aerosols could even account for as high as 80% [2, 3]. WSOC in the atmosphere has caused increasing attention for their important roles in haze pollution and new particles formation due to their specific physical and chemical properties [4, 5].

Saccharides are important substances of WSOC in aerosols, which account for 13%-26% mass of continental aerosols, and 63% mass of marine aerosols [6]. The atmospheric saccharides mainly contain three species: anhydrosaccharides, primary saccharides (monosaccharides and disaccharides), and saccharide alcohols.

Anhydrosaccharides mainly include levoglucosan, mannosan and galactosan, which originate from primarily emissions during the process of biomass burning, and levoglucosan has been widely used as an effective tracer for biomass burning emission [7].
Primary saccharides usually include monosaccharides (glucose, fructose) and disaccharides (sucrose, trehalose), which commonly exist in primary biological aerosol particles (PBAPs) emitted from microorganisms, fungal spores, pollens, biological crusts, lichens and other like plant or animal fragments [8]. Fructose and glucose from the degradation of the microorganisms in the soil could also re-suspend together with the soil dust by wind or some agricultural activities, therefore, fructose and glucose are proposed as tracers for soil suspension [9]. Saccharide alcohols, including mannitol, arabitol, and sorbitol, are mainly come from fungal spores, especially for mannitol and arabitol, which could account for more than 50% of the dry weight of fungal mycelium, thus, saccharide alcohols could be used as tracers for fungal spores [10].

Biomass burning was a worldwide common source of air pollution [11-14]. Levoglucosan in ambient air was usually high in cold seasons due to the heating demand. Bond et al. reported that about 60% of the primary pyrogenic OC were resulted from wood combustion in Europe[15], and the contribution of biomass burning emissions to OC was 45%±12% during the rice-harvest period in Korea [13]. In contrast, saccharides from biological sources showed the highest level in April (the spring bloom season) at Jeju Island, and sucrose contributed to as high as 80% of the total saccharides [16]. Primary saccharides (sucrose, fructose, glucose) showed unimodal distribution with dominant peak occurring in the coarse-particle, while anhydrosaccharides were more likely exist in fine particles [17]. Up to Now, studies about saccharides was mainly focused on levoglucosan for the purpose of evaluating the impact of biomass burning on the air pollution, but information related to the other saccharides, especially those from biological derivations, was still limited, and the characteristics of saccharides during the periods of variable pollution level was lack. However, with the substantially reduction of pollutants emitted from industrial process, the contribution of natural sources and the agricultural emissions to air pollution, especially the PBAPs, has been increasingly emerging and highlight [18-20].

Based on the determination of the chemical species in PM$_{2.5}$ of Shanghai, this study gave detailed information of saccharides in the atmospheric particle matters in urban areas, demonstrated their seasonal distributions, emission sources, and the affected factors, especially for those from biological sources. The characteristics of saccharides were also discussed under different levels of fine particulate pollution.

2. Experiments

2.1. Sampling

The sampling site (31.3°N,121.49°E) in this study is on the roof (20m) of No.4 teaching building on the campus of Fudan University in Yangpu District of Shanghai (Figure 1). It is considered as a representative urban site due to the mixing anthropogenic emission sources of industries, vehicle transportation, biomass burning, and so on [21]. The predominant wind directions in summer and winter are southeasterly and northwesterly, which is influenced by the Asian Monsoon [22].

The sampling period was between March 18, 2013 to January 22, 2014, and the duration of March 18 to April 26, July 16 to August 17, October 29 to November 29, and November 30 to January 22, 2014 was considered to be spring, summer, autumn and winter, respectively. PM$_{2.5}$ sample was collected on the Quartz filters under a medium flow rate of 100L/min by a PM$_{2.5}$ sampler (HY-100c, Qingdao, Hengyuan), the duration time for each sample was usually for 24h.
2.2. Chemical Analysis

A quarter of the sampled quartz filter was shredded and ultrasonically extracted three times with 20ml dichloromethane/methanol (V/V, 1:1), and the extracting solution was combined together, and then a mixture of methyl-β-D-xylanopyranoside (MXP) and cis-ketopinic acid (KPA) was added as internal/recovery standards. After being concentrated to about 1ml with a rotary evaporator (IKA, RV10, Germany), the samples were filtered through quartz wool in glass droppers, and the filtrate was blown to near dry using a nitrogen blowing instrument (Anpel, DC-1 2-RT). Derivatization reaction was then carried out by adding 100μl N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, with 1% trimethylchlorosilane as a catalyst) and 20 ml anhydrous pyridine at 75°C for 45 min using a dry bath (MIU, DTH-100). The reaction products were determined with GC-MS (Agilent, 7890GC/5975 MSD, equipped with DB-5MS capillary column (30m×0.25m×0.25μm), and hexamethylbenzene was added as internal standards. The temperature programming was initially at 60°C for 2 min, then increased to 300°C at a rate of 5°C min-1 and held for 10min. The MS was operated in El mode at 70ev with a scan range of 50-550 amu. The temperature of the injection port was 290°C, and the inlet quantity was 1 μl, the detail procedure were available in [23].

The chemicals in this study include: dichloromethane (HPLC grade, CNW), methanol (HPLC grade, CNW) and hexane (HPLC grade, 95%, CNW); Levoglucosan (>99%), Mannosan (>98%), D(-)-Fructose (>99%), α-D(+) Glucose (>99%), D(+) Arabitol (>99%), D(+) Mannitol (99%) and D(-) Sorbitol (>98%); BSTFA (>99%) and TMCS, anhydrous pyridine (99.5%, moisture content less than 0.005%, Molecular sieve).

2.3. QA/QC

Before sampling, the quartz filters were wrapped in aluminized paper and then prebaked at 550°C in muffle furnace for 4h. All empty and sampled filters were placed within plastic bags and stored at -20°C in refrigerator before sampling or being analyzed. After being flushed with chromic acid lotion, tap water and deionized water successively, all the glass vessels were dried at 120°C for
5 hours and then baked at 450 °C for 4h. To ensure the veracity of the experiments, field blanks were collected for each season with the same sampling operation procedure but without pump on, and the blanks were treated similarly to the sample filter to conduct the solvent and instrument blank as well. To ensure the stable operation of the instrument, 1 standard sample was injected after per 20 samples.

2.4. Multiple statistical analysis

2.4.1. Backward trajectory analysis

To better evaluate the contributions of air masses from different origins on saccharides in Shanghai, 48 h backward trajectory analyses with fire spots were performed from the sampling site at a height of 500 ma.s.l. by using the with the model of HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) (http://www.arl.noaa.gov/ready/hysplit4.html). Burning activities were illustrated by fire spots, and the datasets were downloaded from MODIS Global Fire Mapping by Fire Information for Resource Management System (FIRMS) (https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms/active-fire-data#ed-firms-fire_emap).

2.4.2. Potential source contribution function (PSCF) analysis

PSCF value was conducted to signify the potential source regions which caused elevation of the concerned pollutant at the receptor site. The PSCF values for the grid cells in the study region are calculated by counting the trajectory segment endpoints that terminate within each cell [24]. The number of endpoints that fall in the i,jth cell is designated nij. The number of endpoints for the same cell having arrival times at the sampling site corresponding to concentrations of target compounds higher than an arbitrarily set criterion is defined to be mij [25]. The PSCF value for the i,jth cell is then defined as

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$$

The higher value of PSCF implies the larger contribution of the region to the sampling site. Since PSCF is a conditional probability, low value of Nij brings more uncertainty of PSCF calculation results. In order to reduce the uncertainty, the weight function Wij was needed [26-29].

$$WPSCF = W_{ij} \times PSCF$$

The weighting function reduced the PSCF values when the total number of the endpoints in a particular cell was less than about three times the average value of the end points per each cell [28].

2.4.3. Positive matrix factorization (PMF) analysis

PMF is used to identify the different sources and the corresponding contribution of atmospheric pollutants. US EPA PMF 5.0 model was used in our study, the principle and operational approaches could be found online in the EPA 5.0 Fundamentals and User Guide (http://www.epa.gov/heasd/products/pmf). Briefly, i and j are used to describe the number of samples and components species, respectively, and then, a matrix X with i by j dimensions was used to identify the concentrations and the source profiles, as shown in (3) [30],

$$x_{ij} = \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij}$$

P was the number of factors, g was the contribution of each factor to each sample, f was the source profile of each source, and eij was the residual concentration for each observation. The
constraint of the result was that no sample can have remarkable negative source contributions, which can be solved by the minimum Q value, as shown in (4), and $u_{ij}$ was the measurement of uncertainty of the $x_{ij}$

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{c_i}{u_{ij}} \right)^2$$  
(4)

3. Results and Discussions

3.1. Concentrations and seasonal variations of saccharides

Seven saccharides were detected during the sampling period, including two species of anhydrosaccharides (levoglucosan and mannosan), two species of monosaccharides (fructose and glucose), three species of saccharide alcohols (mannitol, arabitol and sorbitol).

Table 1 showed the concentrations of the seven saccharides in PM$_{2.5}$ samples obtained in Shanghai during 2013. The total saccharides showed significant fluctuation with daily concentration ranging from 15.2 ng/m$^3$ to 1752.8 ng/m$^3$. Annual average concentration of total saccharides (383.8 ng/m$^3$) in Shanghai was lower than those in Beijing (600 ng/m$^3$) and Rajim (10166 ng/m$^3$) (Table 2), which might be the domestic heating and some wood burning in the northern part of China and the heavy wild biomass burning in India. However, the levels of total saccharides in Shanghai were still higher than some sites, such as an urban site (6.2 ng/m$^3$) and a rural site (38.8 ng/m$^3$) of Po valley in northern Italy (Table 2). Total saccharides showed obvious seasonal variation, with the average concentrations were 169.8 ng/m$^3$, 300.5 ng/m$^3$, 288.4 ng/m$^3$, and 688 ng/m$^3$ in spring, summer, autumn and winter, respectively.

Table 1. Annual concentration range and mean value of measured saccharides (ng/m$^3$) in PM$_{2.5}$ samples in four seasons of Shanghai.

<table>
<thead>
<tr>
<th></th>
<th>spring</th>
<th>summer</th>
<th>autumn</th>
<th>winter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>range</td>
<td>average</td>
<td>range</td>
<td>average</td>
</tr>
<tr>
<td>levoglucosan</td>
<td>5.3-142.7</td>
<td>66.0</td>
<td>2.4-195.9</td>
<td>46.5</td>
</tr>
<tr>
<td>mannosan</td>
<td>1.1-29.1</td>
<td>13.4</td>
<td>0.5-40.8</td>
<td>9.7</td>
</tr>
<tr>
<td>Total burning</td>
<td>6.4-171.8</td>
<td>79.4</td>
<td>2.9-236.8</td>
<td>56.1</td>
</tr>
<tr>
<td>fructose</td>
<td>3.4-36.1</td>
<td>19.2</td>
<td>1.2-189.9</td>
<td>35.5</td>
</tr>
<tr>
<td>glucose</td>
<td>2.0-13.0</td>
<td>6.9</td>
<td>0.6-56.1</td>
<td>14.9</td>
</tr>
<tr>
<td>arabitol</td>
<td>0.8-17.6</td>
<td>5.3</td>
<td>0.4-58.9</td>
<td>14.9</td>
</tr>
<tr>
<td>mannitol</td>
<td>3.0-88.1</td>
<td>25.3</td>
<td>4.2-706.5</td>
<td>172.7</td>
</tr>
<tr>
<td>sorbitol</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.1-15.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Total</td>
<td>7.8-153.9</td>
<td>53.7</td>
<td>6.5-1026.9</td>
<td>211.4</td>
</tr>
<tr>
<td>Total</td>
<td>37.5-343.6</td>
<td>169.8</td>
<td>15.2-1423.8</td>
<td>300.5</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>46.5-287.3</td>
<td>94.5</td>
<td>22.6-205.3</td>
<td>62.8</td>
</tr>
<tr>
<td>TS / PM$_{2.5}$</td>
<td>0.04-0.3%</td>
<td>0.1%</td>
<td>0.03-0.8%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

n.d.: has not been detected
Table 2. Comparison of saccharides in this study with that reported in literatures

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Site type</th>
<th>Sampling time</th>
<th>Partic Concentration</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS, Bologna, Italy</td>
<td>urban</td>
<td>June,2012-May,2013</td>
<td>PM$_{2.5}$ 6.2(0.6-16.4)</td>
<td>[31]</td>
</tr>
<tr>
<td>San Pietro Capofiume,</td>
<td>rural</td>
<td>June,2012-May,2013</td>
<td>PM$_{2.5}$ 38.8(0.9-200.4)</td>
<td>[32]</td>
</tr>
<tr>
<td>Rajim, India</td>
<td>rural</td>
<td>October-November</td>
<td>PM$_{2.5}$ 10166(47811-17979)</td>
<td>[32]</td>
</tr>
<tr>
<td>Pingtung, Taiwan</td>
<td>Remote coastal environment(140 m from the)</td>
<td>February-April,2013</td>
<td>PM$_{2.5}$ 589.5</td>
<td>[17]</td>
</tr>
<tr>
<td>THU, Beijing</td>
<td>Urban</td>
<td>Nov,2010-Oct,2011</td>
<td>PM$_{2.5}$ 600.0(66.1-389.1)</td>
<td>[33]</td>
</tr>
<tr>
<td>Fudan, Shanghai</td>
<td>urban</td>
<td>March, 2013-Jan, 2014</td>
<td>PM$_{2.5}$ 383.8(15.2-1752.8)</td>
<td>This study</td>
</tr>
</tbody>
</table>

For the sake of convenience, anhydrosaccharides were defined as Total burning for their burning sources, while monosaccharides and saccharide alcohols were defined as Total biological for their biological sources. The concentrations of Total burning were in the range of 2.9 to 1407.4 ng/m$^3$ (average 228 ng/m$^3$), while 4.0 to 1026.5 ng/m$^3$ (average 117 ng/m$^3$) for Total biological. Total burning contributed 59.4% to the total saccharides, being slightly higher than Total biological, suggesting that biological activities were important sources for saccharides in Shanghai.

3.1.1. Anhydrosaccharides

Anhydrosaccharides were the most abundant species of saccharides, among which, the annual mean value of levoglucosan reach 180.7 ng/m$^3$ and contributed 47.1% to the total saccharides. However, also being as one of anhydrosaccharides, mannosan was relatively low, and its annual mean value was only 48.8 ng/m$^3$, accounting for 12.7% of the total saccharides (Figure 2).
Figure 2. Daily concentrations of seven saccharides in PM$_{2.5}$ (The areas separated by dotted lines indicate the four seasons of spring, summer, autumn and winter)

Similar to the previous studies, anhydrosaccharides exhibited pronounced seasonal variations in Shanghai with high concentrations in cold seasons and low concentrations in warm seasons as showed in Figure 3. The contribution of the anhydrosaccharides in autumn and winter was 62.7% and 70.4%, and decreased to 46.8% and 18.7% in spring and summer. High levels of anhydrosaccharides in autumn and winter were accord with the fact of open-burning of biomass waste during harvest season and heating demand in cold period. The mean concentration of levoglucosan reached 392.2 ng/m$^3$ in winter, which was almost a magnitude higher than that in summer and spring. The significantly high level of levoglucosan in winter and autumn, revealed the impact of biomass burning emission on urban air quality in addition to the regional transport. Except for heating demand, open burning of crop residues during the post-harvest months (October-November) was still be conducted frequently despite prohibition by government, resulting in high concentrations of levoglucosan in the ambient atmosphere [34, 35]. Mannosan, the isomer of levoglucosan was relatively low compared to levoglucosan with 126.5 ng/m$^3$ in winter and 9.2 ng/m$^3$ in summer. The correlation coefficient between the two anhydrosaccharides reached 0.73, indicating the similar burning sources. According to previous report, levoglucosan and mannosan were originated from different biomass materials: levoglucosan came from thermal decomposition of cellulose usually existing in hard wood (angiosperm), while from hemicellulose [36] mainly in soft wood for mannosan (gymnosperm), and the ratio of levoglucosan / mannosan (L/M) could be used to identify the sources of biomass materials.
Previous studies demonstrated the L/M ratios from hardwood burning were in a range of 15-25, while those of softwood were 3-10 [37-39]. Generally, high values of L/M represented more hardwood biomass burning involved. L/M ratios of 40-42 were found in the smoke aerosols collected from burning of rice straw in chamber [40] and 40-46 from open field burning of wheat straw in the North China Plain [16].

L/M values in this study was relatively low, with 7.26 in winter and 11.29 in autumn, L/M values in autumn was higher than that in winter revealed an increasing of hardwood burning, which was in consistence with the fact that opening burning of rice straw, the typical specie of hard wood, was conducted during harvest season of September to November in China.

Recent studies have raised doubts about the stability of levoglucosan during long-distance transmission [41], because levoglucosan could react with free radicals in the atmosphere. Hoffmann et al. found levoglucosan could be resolved in the presence of strong oxidizers[42]. After determined the seasonal variations of the levoglucosan over the Pacific Northwest and compared to the results of model prediction, Mochida et al. found that the measured data was significantly lower than the model predicted concentration, which might be attributed to the oxidative decomposition of levoglucosan by reaction with OH radicals[43]. During the period of this study, the radiation in spring and summer was obviously higher than that in autumn and winter (Figure 4), and concentration of levoglucosan was significant negative correlation with ozone (Figure S1), indicating that the decrease of levoglucosan was likely attributed to the degradation under the strong oxidizing environment in spring and summer. Therefore, the contribution of biomass burning in summer might be underestimated while levoglucosan was used as tracer.

3.1.2. Saccharide alcohol

Saccharide alcohols were important parts of the saccharides as well, mannitol, sorbitol and arabitol contributed 15.1%, 9.2% and 2.3% to total saccharides, and the annual mean value of the three species was 57.8 ng/m³, 35.7 ng/m³ and 8.7 ng/m³, respectively. In contrast to the highest level of anhydrosaccharides in winter, saccharide alcohols contributed the most proportion in summer, reaching 53.6% to total saccharides, while 16.3% and 14.5% in spring and autumn, but only 11.0% in winter (Figure 3). The mean concentration of Mannitol in summer (172.7ng/m³) was much higher than that in winter (37.6 ng/m³), and the similar pattern also appeared for arabitol with 14.9 ng/m³ in
summer and 8.3 ng/m$^3$ in winter. Saccharide alcohols were mainly produced by fungal spores and some synergistic effects of photosynthesis, which usually show high activities in the case of high temperature and enough light. Moreover, research showed that mannitol was the product of plant resistance[44], for example, extreme high temperature caused the water deficit, and mannitol was produced to regulate osmotic pressure of cells to detect and respond to the environment[45]. In Shanghai, the mean temperature in summer was 33.2 ℃, while only 6.69 ℃ in winter, and the solar radiation intensity was 257.2 W/m$^2$ and 303.7 W/m$^2$ in spring and summer, being much higher than 151.6 W/m$^2$ in autumn and 154.6 W/m$^2$ in winter (Figure 4). The significantly high concentrations of Saccharide alcohols in summertime suggested that the emission of saccharide alcohols from biological sources was restrained by the meteorological conditions, such as temperatures, rainfall and illumination intensity, etc.

Different from mannitol and arabitol, sorbitol showed different seasonal variation, with the highest concentration occurred in winter. Two possible reasons were considered. For one thing, sorbitol was more likely to exist in coarse particles, Peng et al. found sorbitol was mainly distributed in the size of 3.2-5.6 μm in spring and summer, and 1.8 μm in winter[23]. Therefore, sorbitol mostly existed in coarse particles in spring, summer, and autumn. However, it was fine particles that were collected in this study. Therefore, the low concentration of sorbitol could be better understood. On the other hand, the sources of the high concentration of sorbitol in winter of this study needs further discussion.

Figure 4. Meteorological conditions of Shanghai in 2013

3.1.3. Monosaccharides

Monosaccharides included fructose, and glucose, of which the annual mean value were 31.3 ng/m$^3$ and 10.9 ng/m$^3$ and contributed 8.2% and 2.8% to total saccharides, respectively (Figure 2). Monosaccharides exhibited similar seasonal variations as saccharide alcohols but showing less
fluctuation, with the highest level of 37.0% occurred in spring, and the contribution in summer and autumn was comparable for 27.7% and 26.3% respectively, while only 15% in winter (Figure 3).

Unlike the significant seasonal variation of anhydrosaccharides and saccharide alcohols, fructose and glucose in the atmosphere were relatively stable, likely attributed to less affected by human activities and the natural conditions, such as temperature and relatively humidity.

3.2. PMF analysis and PSCF analysis

Positive matrix factorization (PMF) analysis and potential source contribution function analysis (PSCF) provide a further investigation of the sources and characterizations of the atmospheric saccharides.

In the PMF analysis, each PMF performance was calculated for 30 times with three to seven factors due to the minimum Q value and the interpretable factors of PMF, and four factors were resolved for the probable sources of atmospheric saccharides in Shanghai, the factor profiles were shown in Figure 5.

Figure 5. PMF factor analysis of saccharides in Shanghai in 2013.

The four factors contributed 46%, 22%, 22%, and 10% to the atmospheric saccharides in Shanghai, respectively. Factor 1 was identified by high levels of levoglucosan (93.2%), and mannosan (86.5%), suggesting the obvious source of biomass burning from crop residue or other biofuels in the local rural areas around Shanghai or regional input. Factor 2 was dominated by saccharide alcohols (72.0% mannitol and 55.8% arabinol), indicating the sources of fungal spores. As mentioned before, saccharide alcohols were mainly produced by fungi [46], mannitol could account for up to 50% of fungal mycelium[10], and spores serve for the fungal reproduction and survival when entering the breeding stage, which were often released by active processes related to osmotic...
pressure and surface-tension catapults [47]. Factor 3 was characterized by fructose (59.2%) and glucose (50.9%), indicating the source of soil suspension. Being abundant in vascular plants, fructose and glucose would be released attributed to diagenetic degradation caused by heterotrophic microorganisms in soil [6]. Soil containing fructose and glucose could be blown up to atmosphere from the dormant or arid land, and agricultural activities could intensify this release, such as tilling in post-harvesting seasons [9]. Factor 4 was dominated by airborne pollens for the reason that fructose (14.3%), glucose (18.8%), arabitol (25.5%), mannitol (10.9%) and sorbitol (19.4%) were relatively average. Pollens are reproductive units of plants, containing those saccharides and saccharide alcohols as nutrition components [48].

In PSCF analysis (Figure 6), the depth of the color reflected the impact of the mass concentration in the region, which could reveal the potential sources of the atmospheric saccharides. PSCF result of levoglucosan and mannosan was consistent that the deeper color mainly existed in Jiangsu province, indicated that the potential sources of anhydrosaccharides in Shanghai was attributed to external input from the northwestern region. Compared to mannosan, the potential sources of levoglucosan distributed a little widely, also extended to Anhui and Zhejiang province.

Figure 6. PSCF analysis of chemical species in PM$_{2.5}$ in Shanghai. (a) Levoglucosan; (b) Mannosan; (c) Mannitol; (d) Arabitol; (e) Sorbitol; (f) Fructose; (g) Glucose

Saccharide alcohols were found to exist mainly in lower plants, such as algae, lichens, fungi, and the barks, branches and leaves of trees [49], and mannitol and arabitol were from fungal spores. Heald and Spracklen[50] found that atmospheric moisture and leaf area index had a significant correlation with the concentration of mannitol. PSCF analysis showed that the potential sources of mannitol and arabitol mainly existed in the regions south of Shanghai, which might be attributed to the adequate plant coverage, together with the relatively high temperature and sufficient moisture in the region, such as Zhejiang province and the southern Anhui. Furthermore, Figure 6(c), Figure 6(d) and Figure 6(e) showed that the concerned saccharide alcohols exhibited variable distribution. The potential sources of mannitol extended to the southern Jiangsu and further northern regions, but the potential source distribution of sorbitol was limited in the northern area of Shanghai. The different distribution for mannitol and arabitol suggested their different fungal spores [51].

The potential source of fructose was mainly in Jiangsu, and glucose existed in amore southerly regions compared to fructose. The reason might be that glucose was more likely to exist in the
nectars and fruits of tropical plants in the regions south to Shanghai [52]. Interestingly, the most potential source of glucose was dominantly from the ocean area, where fewer known to be present. The probable sources might be from the algae and lichens and other lower plants by the sea, which needs further study to investigate.

3.3. The formation process of high level of levoglucosan

A process of levoglucosan with significant fluctuation was detected, of which the concentration reached 285.7 ng/m³ from November 4 to 9, being much higher than the mean value of 165.7 ng/m³ in autumn. The average L/M value of the period was 26.5, especially for the November 7 and November 9, L/M values were 64.8 and 56.7, a little higher than the ratios of 40-42 from burning of rice straw in chamber [40] and open field burning of wheat straw [16]. Therefore, the suddenly increase of saccharide was due to the treating of crop waste by open burning directly in the field.

The backward trajectories and the distribution of fire spots during the period were shown in Figure 7, which indicated that the air mass transported through the areas of intensive fire spots. From November 4, the number of the fire spots increased gradually, especially on November 6 and 7, the concentration of levoglucosan was highest as 823.6 ng/m³ and 425.9 ng/m³ on those two days, which indicated that the concentration of levoglucosan was consistent with the variations of the fire spot intense. Specifically, the air mass was from the northern part of Shanghai, and the pollutants transformed to Shanghai over the sea on November 4 and 5, with the concentration of levoglucosan of 94.3 ng/m³ and 95.0 ng/m³, and the number of fire spots sharply increase on November 6, the air mass trajectory hovered in Shanghai, which indicated the unfavorable climate conditions, therefore the concentration of levoglucosan reached the highest value of 823.6 ng/m³, the trajectory on November 7 was from the west part of Shanghai, such as Anhui and Henan, was consistent with the distribution of fire spots, and the concentration of levoglucosan decreased but still a high value of 425.9 ng/m³, the meteorological conditions improved on November 8, and the trajectory of November 9 was from the southwest part of Shanghai, such as Zhejiang, Jiangxi, and influenced by the local fire spots. The conclusion is that in addition to the local pollution, the present biomass burning event mainly came from the external transmission, mainly from the southwest of Shanghai, and the influence in the north is relatively small.
349 Figure 7. Fire spots distribution combined with the 48-h backward trajectory analysis during the period.

350

351 3.4. The characterization of saccharides under haze episode

352 Over the past decades, China has suffered serious air pollutions [53, 54], especially in those most developed and highly populated regions, such as Yangtze River Delta (YRD), the Pearl River Delta (PRD), and Beijing-Tianjin-Hebei (BTH) [55]. The haze pollution, characterized by low visibility attributed to light extinction caused by high levels of particulate matter, especially fine particles enriched with anthropogenic pollutants [56, 57]. Severe haze with long duration and wide area China occurred in December 2013, which provided a chance to track the variation of aerosol particles and the constituents. During the pollution period, hourly maximum concentrations of PM$_{2.5}$ in Shanghai exceeded 600 $\mu$g/m$^3$. Quantities of researches have focused on the chemical components, temporal variation of inorganic ions and elements during the haze particles [58, 59]. However, few information related to saccharides was available during the pollution period [60].

363 The compositions of the saccharide alcohols showed opposite trends compared to particulate matters. During the period when the averaged concentration of PM$_{2.5}$ was lower than 100
ng/m$^3$ (named clear period), the concentrations of arabitol, mannitol and sorbitol were 3.78 ng/m$^3$, 29.07 ng/m$^3$ and 44.16 ng/m$^3$, respectively, but increased to 8.9 ng/m$^3$, 44.8 ng/m$^3$ and 112.1 ng/m$^3$, when concentration of PM$_{2.5}$ was above 150 ng/m$^3$ (named haze period). The obvious reduction of saccharide alcohols during heavy PM$_{2.5}$ pollution period suggested the inverse influence of haze pollution on biological activities, and then might further result in the cut of agricultural production. Some studies had found that the average level of microbial activity was 100.33 ng/m$^3$ sodium fluorescein on sunny days, and decreased to 56.53 ng/m$^3$ sodium fluorescein on haze days. When the haze was mixed with fog for several days, the microbial activity reduced to 37.7% of the level of sunny days [61]. Studies also found haze may damage the hierarchy and functions in the ecosystem, lead to the loss of the crops, and then reduce biodiversity and even damage the biological chain. The reduction of biological activity was demonstrated from the perspective of saccharides in this study.

The two monosaccharides showed similar trend as PM$_{2.5}$ did, and the concentrations of fructose and glucose were 35.7 ng/m$^3$ and 11.8 ng/m$^3$ during the haze period, while only 13.5 ng/m$^3$ and 12.0 ng/m$^3$ in the clear period. Being markers of soil suspension, the concentrations of fructose and glucose should increase in the atmosphere with the increasing of windy speed. However, the mean wind speed was comparable in the two periods, suggested there likely exist other reason for the difference.

The concentrations of levoglucosan in the two periods were 379.1 ng/m$^3$ and 414.3 ng/m$^3$. Similarly, mannosan was 133.3 ng/m$^3$ and 146.7 ng/m$^3$ of the two periods, respectively. Anhydrosaccharides had showed no obvious difference suggested that biomass burning was not the trigger factor of the haze in the winter, 2013 in China. Further investigation was about the SNA (sulfate, nitrate and ammonium) in the two periods. The mean concentration of sulfate in heavy haze period was 23.1 $\mu$g/m$^3$, which was 2.7 times higher than the clear period (8.6 $\mu$g/m$^3$). The nitrate and ammonium were consistent with sulfate.

4. Conclusions

In this study, a one-year long PM$_{2.5}$ samples were collected to identify the compositions, sources, and seasonal variations of the atmospheric saccharides, and the characteristics of saccharides under different levels of pollution were also discussed. The concentration of the total saccharides was in a range of 15.2 ng/m$^3$ to 1752.8 ng/m$^3$ (average 383.8 ng/m$^3$) during the whole year, with high concentrations of anhydrosaccharides from burning sources in cold seasons, high concentrations of saccharides alcohols from biological sources in warm seasons. Four factors of biomass burning, fungal spores, soil suspension, and airborne pollens were obtained through PMF analysis with contributions of 46%, 22%, 22%, 10% of the atmospheric saccharides in Shanghai. Results of PSCF analysis indicated that levoglucosan and mannosan had similar potential sources in the northern regions of Shanghai, and mannitol almost existed in the southern regions of Shanghai as the higher temperature and humidity, and the rest of saccharides alcohols and monosaccharides had different distributions for the different species and quantities. Resolution of backward trajectory and fire points showed the process of high concentrations of levoglucosan due to the biomass burnings. Concentrations of anhydrosaccharides showed relatively stable under the conditions of clear and pollution period while saccharide alcohols exhibit an obvious variation, indicated that biomass burning was not the core reason of the haze pollution, however, haze air pollution could lead to a significant reduction of biomass activity from the perspective of the saccharide alcohols.
Table S1: List of days haze (>150 μg/m³, 17 days) and clear (<100 μg/m³, 8 days) period.

<table>
<thead>
<tr>
<th>Date</th>
<th>PM2.5(μg/m³)</th>
</tr>
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<tbody>
<tr>
<td>Haze</td>
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</tr>
<tr>
<td>12/6/13</td>
<td>416.5</td>
</tr>
<tr>
<td>12/5/13</td>
<td>331.5</td>
</tr>
<tr>
<td>12/1/13</td>
<td>285.6</td>
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<tr>
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<tr>
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<td>215.3</td>
</tr>
<tr>
<td>12/2/13</td>
<td>213.4</td>
</tr>
<tr>
<td>1/13/14</td>
<td>206.2</td>
</tr>
<tr>
<td>12/3/13</td>
<td>204.4</td>
</tr>
<tr>
<td>12/7/13</td>
<td>190.0</td>
</tr>
<tr>
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</tr>
<tr>
<td>1/20/14</td>
<td>187.2</td>
</tr>
<tr>
<td>1/3/14</td>
<td>185.3</td>
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<tr>
<td>Clear</td>
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<tr>
<td>1/4/14</td>
<td>56.9</td>
</tr>
</tbody>
</table>

Figure S1: The negative correlation between levoglucosan (ng/m³) and O₃(μg/m³)
Author Contributions: Mengxin Xiao conducted the experiments and wrote this paper; Qiongzhen Wang made suggestions for this paper; Xiaofei Qin and Guangyuan Yu conducted the sampling activities; Congrui Deng reviewed the general idea in this paper. All authors have approved the final manuscript.

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