Using Polyurethane Foam-based Passive Air Sampling Technique to Monitor Monosaccharides at a Regional Scale

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Monosaccharides are important tracers of pollution aerosol from biomass burning. Air sampling of monosaccharides is often conducted using active samplers. However, applicability of sampling monosaccharides using polyurethane foam passive air samplers (PUF-PASs) has not been investigated, since passive samplers are often applied to monitor semi-volatile organic contaminants in large scale and remote area. Our study successfully collected atmospheric monosaccharides using PUF-PASs, providing a valuable tool for monosaccharides sampling. PUF-PAS sampling rates for individual monosaccharides were calibrated using an active sampler for 92 days, and were 1.1, 1.5 and 1.1 m$^3$/d for levoglucosan, mannosan and galactosan, respectively. Degradation of monosaccharides in PUF-PAS was demonstrated to be negligible by spike test of $^{13}$C-labeled levoglucosan. Furthermore, passive sampling was carried out at 11 sites in Pearl River Delta of Southern China during January to April and July to September in 2015. Monosaccharide concentrations derived from PUF-PASs were comparable with the reported data obtained by active sampling, demonstrating that PUF-PAS approach is valid for monosaccharides monitoring. Based on our approach, we found that there is a clear correlation between the monosaccharide concentrations and the MODIS fire activities during January-April.
1. INTRODUCTION

Biomass burning (BB), particularly open biomass burning events such as land clearing, agricultural waste burning, prescribed burning, field burning, and wildfires,\(^1\)\(^2\) is of global concern for its primary source of pollutant emissions into the atmosphere across the world, and significant impact on air quality and radiation balance of atmosphere.\(^3\)\(^-\)\(^5\) To track contribution of BB to atmospheric pollutants relative to other sources, molecular markers can be used. Levoglucosan, together with its isomers mannosan and galactosan, have been widely used as molecular markers of emissions from BB,\(^6\) due to advantages such as large quantities emitted, and little interference from other sources.\(^7\)\(^-\)\(^9\) The monosaccharides are degradation products of cellulose, occurring as specific indicators of BB.\(^7\)

Atmospheric levoglucosan sampling was commonly carried out by active air samplers (AAS).\(^10\)\(^-\)\(^12\) Most studies focused on levoglucosan in particle phase collected by AAS, while the gas phase was overlooked.\(^13\)\(^-\)\(^15\) However, levoglucosan was supposed to be a semi-volatile organic compound (SVOC),\(^13\)\(^,\)\(^16\) partitioning of which in gas phase could be significant under specific environmental conditions.\(^13\)\(^,\)\(^17\)\(^-\)\(^21\) Laboratory studies reported a vapor pressure of \(\sim 2.0 \times 10^{-4}\) Pa and an estimated octanol-air partitioning coefficient \((K_{OA})\) of \(\sim 1 \times 10^{10}\) of this compound at 298 K.\(^13\)\(^,\)\(^14\)\(^,\)\(^18\) May et al. (2012) reported that at least 10% appreciable gas quantities of levoglucosan were found under typical atmospheric conditions (with organic aerosol (OA) concentration of \(C_{OA}=5\) µg/m\(^3\) and temperature of 298 K). Model results even showed that almost 95% of levoglucosan existed in the gas phase during wildfires in the summertime, while the value decreased to less than 10% during wood burning in colder winter temperature.\(^13\) Recently, a field study on gas/particle partitioning of
levoglucosan at an urban site using AAS observed that gas-phase concentrations were 0.02-3 times comparing with the ones in the particle phase during the sampling period.\textsuperscript{15}

In the last two decades, passive air samplers (PAS) were widely used in the sampling of SVOCs, such as PCBs, PBDEs, and PAHs.\textsuperscript{19-24} Due to the facts including the small size, the low cost, the portability, the easy installation, the power-free operation and the convenient maintenance of PAS, it is more applicable for a large-scale and a long-period sampling comparing with active samplers.\textsuperscript{25, 26} However, as for its application in a sampling of levoglucosan in air, to our knowledge, has not been reported. Polyurethane foam (PUF) disk based on PAS (PUF-PAS) is the most popular PAS type.\textsuperscript{22, 27-30} PUF-PAS was originally used to collect gas-phase compounds, but there was an application in both gas and particle phase, or solely particle phase samplings nowadays.\textsuperscript{31} A good agreement has been found between the concentrations and size distributions for the particles less than 2.5 µm measured inside and outside of several popular PUF-PAS designs.\textsuperscript{32} Thus, not only gas-phase chemicals but also particles less than 2 µm typically represented by 0.3-0.5 µm can be sampled by a PUF disk because of the similar aerodynamic behavior to gases.\textsuperscript{25, 26, 33} Since the diameter of ambient particle-phase levoglucosan is smaller than 0.44 µm when BB tracers originate directly from the source emissions, while typically ranging from 0.44 to 1.0 µm when it is aged and sampled away from combustion sources.\textsuperscript{34, 35} It is also reported that the concentrations of levoglucosan in PM\textsubscript{1} and PM\textsubscript{2.5} were comparable, either of them accounting for at least 50% of PM\textsubscript{10} in the PRD region.\textsuperscript{36} Therefore, the application of PUF-PAS should be feasible for collecting both gas- and particle-phase monosaccharides.
Sampling rates of PUF-PAS are influenced by physicochemical properties of target compounds, superficial area and volume of PUF, design of sampler, atmospheric conditions (e.g. photooxidation conditions, ambient temperature, background OA concentration and etc.) and meteorological parameters (e.g. wind speed, temperature, humidity, aerosol concentration and etc.). Sampling rates could be varied in the range of 0.7-8 m$^3$/d for particle associated SVOCs, such as polycyclic aromatic hydrocarbons (PAHs).

In the present work, we determined the sampling rates of levoglucosan and its isomers using a PUF-PAS consisting of a double-dome sampling chamber. PUF-PAS in the same design has been used in previous studies on persistent organic pollutants (POPs). Sampling rates of PUF-PAS were calibrated by a co-deployed AAS for 92 days. Degradation of levoglucosan during passive sampling was monitored by spiking of $^{13}$C$_6$ levoglucosan. Finally, two campaigns of passive sampling were carried out to monitor monosaccharides in the air of the Pearl River Delta (PRD) region in China. Levoglucosan levels derived by PUF-PAS were compared with literature AAS results from the same region, as well as regional satellite fire counts results.

2. MATERIALS AND METHODS

2.1 Calibration Exercise for Monosaccharides

Passive samplers used in this study consisted of a PUF disc (14.0 cm diameter, 1.35 cm thickness, 365 cm$^2$ surface area, 3.40 g mass, 207 cm$^3$ volume, and 0.0213 g/cm$^3$ density), which was housed in two stainless steel domed chambers in order to dampen the effect of wind speed on the uptake rate and to protect the PUF disks from precipitation, direct particle deposition and ultraviolet radiation. More detailed information of the sampler were shown in Table S1 of the supporting information (SI). The PUF disks were precleaned by extraction with a mixture of
methanol and dichloromethane (DCM) (7:93, v/v) for 36 h. Chambers were precleaned and solvent-rinsed with methanol beforehand. A total of 15 passive samplers were set up and deployed from the 26th of July to the 26th of October in 2016 for over a 92 d period. The sampling site was on the roof of an office building (~30 m) at the Guangzhou Institute of Geochemistry, located at an urban site in Guangzhou, China, without any obvious point emission sources nearby. During the calibration exercise, the daily temperature ranged from 25 °C to 31 °C, with an average of 29±1.6 °C. The daily relative humidity (RH) ranged from 61% to 85%, with an average of 73±6.8%. Other information on basic environmental and meteorological parameters during the calibration exercise was shown in Table S2. PUF-PASs were hung approximately 1.5 m above the ground in an open area. All the PUF disks were pretreated with 14 µg of 13C6 levoglucosan as a degradation reference prior to deployment. Every three parallel PUF disks were collected at 16 d, 30 d, 50 d, 73 d, and 92 d intervals over the period. (Table S3) In the meantime, active air sampling was conducted continuously alongside the passive sampling throughout the calibration exercise. The AAS was set at an identical height for the deployment of the passive sampler. A total of 16 pairs of total suspended particle (TSP) samples were collected on prebaked (450 °C, 4-5 h, muffle furnace) quartz fiber filters (QFFs, 18×10.5 cm²), and gas samples were collected by the PUF plugs. The samples were collected for a 3-7 day duration at a stable flow rate of 300 L/min. (Table S3) After sampling, all folded QFFs, PUF plugs and PUF disks were wrapped in aluminum foil, sealed in PE bags and stored in a refrigerator at -20 °C before analysis. It should be noted that because of the unavoidable factors including the interruption of a power supply, the super heavy rainfall, and the typhoon, the active sampling time did not fully match the retrieve time of PUF-PAS (Table S3). For example, the passive sampling duration of the 1st period was from 26th July to 11th August, its corresponding
active samples were Number 1-3. In this case, the average concentrations of monosaccharides derived by active sampling during the corresponding deployment time of PUF-PAS were used as the referenced air concentrations during the calibration exercise.

**2.2 Field Sampling in the PRD**

Eleven locations belonging to the environmental monitoring network of Guangdong Provincial Environmental Monitoring Center were selected with the intention of avoiding point sources contamination. It includes 5 urban sites (ZQ (Zhaoqing), TH (Tianhe), FS (Foshan), ZH (Zhuhai) and SZ (Shenzhen)), 5 rural or suburban sites (CH (Conghua), JL (Jiulong), JM (Jiangmen), JGW (Jinguowan) and BL (Boluo)), and 1 background site (TJ (Tianjin Mountain)) (Figure 1). Details of each sampling site and basic related parameters are given in Table S4 and Table S5. Samplers were assembled at the deployment sites to avoid contamination during transit. PUF-PASs were deployed for approximately 58 days in the transitional period of winter and Jan-Apr (January 30 to April 15) and approximately 66 days in Jul-Sep (July 6 to September 16) of 2015. After deployment, the PUF disks were retrieved, resealed, and returned to Guangzhou, where they were stored and kept frozen until extraction and analysis.

**2.3 Monosaccharides analysis**

Monosaccharides collected on QFFs and PUF disks were analyzed by validated methods with details provided in Section 1 of the SI. Briefly, the aliquots for the QFFs, PUF plugs and PUF disk samples were spiked with methyl-β-L-xylanopyranoside (MXP) or $^{13}$C$_6$ levoglucosan as internal standards. Samplers were then Soxhlet extracted for 36 h, concentrated with a rotary evaporator and pure nitrogen gas and derivatized by N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% of trimethylsilyl chloride and pyridine (2:1, v/v) at 70 °C for 1 h. The derivatives were dried by
nitrogen and diluted by the addition of n-hexane prior to the quantification by gas chromatography-mass spectrometry (GC-MS).

2.4 QA/QC

A total of 2 sets of field blanks consisted of QFFs, PUF disks and plugs for the calibration exercise, 2 field blanks of PUF disks for the PRD sampling campaigns, and 7 procedural blanks were extracted and analyzed in the same manner as the samples. The analytes in the laboratory and the field blanks were significantly lower than the concentration of the field samples. For the field blanks, only small amounts of monosaccharides were detected in PUF plug and PUF disk, with average values lower than 220, 10, and 28 ng/sample for levoglucosan, mannosan and galactosan, respectively, which were typically less than 5% of sample amounts. Field blank data have been subtracted from all the samples.

To evaluate recoveries during pretreatment procedures, $^{13}$C$_6$ levoglucosan was spiked in the blank samples as a surrogate, then 1000 ng of MXP and hexamethylbenzene (HMB) were added as quantification internal standards before derivatization and before injection, respectively. The recovery of $^{13}$C$_6$ levoglucosan ranged from 85% to 150% for PUF disks when using HMB as the internal standard. When taking the derivatization efficiency into consideration, the recovery ranged from 95% to 110% for QFFs and from 52 to 130% for PUF plugs and disks when using MXP as the internal standard. The method detection limit (MDL) was defined as the average of the blanks plus 3 times the standard deviation, which was 97, 22 and 5.7 ng for levoglucosan, mannosan and galactosan, respectively. All the reported results were corrected with surrogate recoveries.

In this study, all the meteorological parameters were obtained from the website of https://www.aqistudy.cn/. Terra MODIS statistics of thermal anomalies/daily fire products
(MOD14A1) were downloaded from

https://ladsweb.modaps.eosdis.nasa.gov/api/v1/productPage/product=MOD14A1.
3 RESULTS AND DISCUSSIONS

3.1 The Feasibility of Using PUF-PAS to Determine Air Concentrations of Monosaccharides

3.1.1 Particle-Phase Fraction of Monosaccharides in the AAS Samples

All the data for the monosaccharides concentrations, including the gas- and the particle-phase concentrations, are summarized in Figure S3, Table S6 and Section 2 of the SI. The particle-phase fraction parameter, \( \phi_p = \frac{C_p}{C_p + C_G} \) (Eq. 2), has often been used to describe the partitioning behavior of SVOCs in air, where \( C_p \) (ng/m\(^3\)) and \( C_G \) (ng/m\(^3\)) are the particle- and gas-phase concentrations of the target compound, respectively. The \( \phi_p \) for levoglucosan varied from 41% (RH=70%) to 97% (RH=70%), with an average value of 78±18% (Table S7 and Figure S4). The \( \phi_p \) for mannosan and galactosan were in the range of 9.3% - 92% and 17% - 78%, with average values of 59±27% and 52±18%, respectively. The ratios of gas- to particle-phase (\( C_G/C_p \)) of levoglucosan ranged from 0.031 to 1.44, with the median value of 0.17 (Table S7), which were comparable to those reported in the previous study (0.02-3.04, 0.23 (median value)) conducted in Denver, Colorado (U.S.), showing that the semi-volatile characteristics of levoglucosan and reporting the non-negligible impact of gas-phase levoglucosan on the total concentration.

Although the significantly high concentrations of primary organic aerosol (POA) (hundreds of \( \mu g \) m\(^{-3}\)) favors the particle phase, particle-phase concentrations from BB sources will be rapidly diluted with a background as POA diffuse, shifting gas-particle partitioning of monosaccharides to the gas-phase. As the gas-phase oxidation can alter the gas-particle equilibrium, particle-phase species will further evaporate to maintain phase equilibrium. Even a small fraction of gas-phase species will induce additional oxidation. Therefore, the \( C_G/C_p \) will change as POA emissions leave the sources.
Considering the atmospheric conditions, particle-phase liquid water has been observed to play the predominant role in the gas/particle partitioning of water-soluble organic matter in the eastern U.S.\textsuperscript{42} In this study, humidity was found to be closely negative related to the total concentration of levoglucosan (p<0.05) and mannosan (p<0.01), as well as the gas- and particle-phases of levoglucosan (p<0.05), implying the high relative humidity would influence the gas-particle partitioning and promote more gas-phase monosaccharides. This might probably due to the solubility of levoglucosan in the liquid water content of aerosol, which was related to humidity.\textsuperscript{43} Likewise, the impact of ambient temperature on $\phi_p$ was negligible due to the small variations in the temperature during the study period.\textsuperscript{44, 45} Thus, the particle phase fraction of monosaccharides in Guangzhou was primarily driven by humidity or particle-phase liquid water. Information about the correlations with other daily basic environmental parameters is shown in Table S8.

### 3.1.2 The Degradation of Monosaccharides in PUF-PAS

In this study, the average recovery of spiked $^{13}$C$_6$ levoglucosan in PUF disks varied from 81±0.0% to 98±1.6% in different retrieval periods (Figure S1), indicating a stability of monosaccharides on PUFs. Degradation can be neglected over a long-time deployment up to 92 days, with the effective protection of PAS from the degradation of atmospheric oxidants in the ambient atmosphere.\textsuperscript{6, 46} Some laboratory studies reported that the semi-volatile molecular markers would rapidly decay (0.2-3.6 days) when undergoing accelerated chemical oxidation under average summertime conditions and different environmental conditions.\textsuperscript{13, 47, 48} However, the previous work has shown that levoglucosan remains stable over a period of around 10 days under the exposure to ambient levels of sulfate acid and some photochemical oxidants, such as ozone and gaseous nitrogen dioxide.\textsuperscript{6} Moreover, the concentrations of oxidants in the real atmosphere are discrepant with those
monitored in laboratory, which might be much lower than the critical values detected under a laboratory condition. For example, levoglucosan is unlikely to undergo significant decay considering winter synoptic conditions and estimated OH concentrations (<1\times10^6 \text{molecules/cm}^3).^{49} Actually, the most atmospheric reactive species had already been reacted to the freshly emitted active monosaccharides prior to collection, making particles less available for further degradations.\textsuperscript{46} Moreover, the structure of PUF-PAS might be helpful for the “reservation” of monosaccharides. The effect of the diffusion of oxidant gases on the PUF-PAS is much slower than the diffusivity in the air and is limited to a <1 cm penetration into the PUF.\textsuperscript{50} Also, the protective structure of the shielded particle made them less available for further degradation.\textsuperscript{46, 51} Therefore, with the protection of the double-domed chambers of PAS, degrading factors were further reduced.\textsuperscript{27} Monosaccharides could be considered stable and hardly re-volatile when they are once collected on the PUF-PAS.

3.1.3 The Accumulation of Monosaccharides in PUF-PAS

The capture of monosaccharides by the PUF-PAS increased linearly over 73 days (Table S3 and Figure S2). The linear uptake stage time was comparable with that during 2-9 weeks for the particle-bound PAHs.\textsuperscript{52} The three monosaccharides in the PUF-PAS likely approached the curvilinear uptake stage after the 73-day exposure. Thus, to maintain linear uptake conditions of passive sampling for monosaccharides, the field sampling time is suggested to be no more than 70 days. The uptake of a target compound by PUF-PAS is based on the following equation:

\[ V_S(dC_S/dt) = k_oA_S(C_A - C_S/K_{SA}) \] (Eq 1), where \( V_S \) is the volume of PUF; \( C_S \) and \( C_A \) are the concentrations of analyte in PUF-PAS and air, respectively; \( k_o \) is the overall mass transfer coefficient; \( A_S \) is the superficial area of PUF; and \( K_{SA} \) is the PUF/air partition coefficient, which is related to
Among these parameters, $V_S$, $A_S$, and $K_{SA}$ are related to the uptake and sampling rates of target compounds by PUF-PAS. The volume ($V_S$) and the superficial area ($A_S$) of PUF used in the current study are as the same as the studies of Shoeib and Harner (2002) and Wilford et al. (2004), while the linear phase region would be different when comparing to other PUFs. As the function of temperature, for nonpolar POPs, $K_{SA}$ has been estimated according to a relationship between $K_{SA}$ and $K_{OA}$, which will increase by a factor of about 3 for every 10 °C drop in temperature, thus increasing the linear phase region of PUF-PAS. Regardless of the polar characteristics of monosaccharides, however, during the calibration exercise, the daily temperature all ranged within 10 °C and the average daily temperature varied within a small range. Thus, the influence of temperature could be ignored.

### 3.1.4 Air Sampling Rates for Monosaccharides

According to Eq1, when the term $C_S/K_{SA}$ is small, it is linear accumulation stage, the equivalent air volumes ($V_{eq}$, m$^3$) of the PAS samples plotted against the given exposure period (d) were based on the following: 
\[
V_{eq}(m^3) = \frac{M}{C_A} = RT \quad (\text{Eq} \ 3)
\]
where $M$ is the daily accumulated mass of target compound collected by each PUF disk during the exposure period (M, ng/d); $C_A$ is the daily air concentration of target compound measured by AAS (gas+particle phase) during the corresponding deployment time of PUF-PAS ($C_A$, ng/m$^3$/d); $T$ is the exposure time of the PUF disk; and $R$ was the sampling rate of PUF disk over the uptake phase (R, m$^3$/d). Each pair of PAS-AAS data for the target compound could be used to build an equation to calculate the $V_{eq}$ for each period, using the above equation. (Table S9)

Linear uptakes of monosaccharides for PUF-PAS over the calibration exercise period were found by good linear correlations between the values of $V_{eq}$ and $T$ within 73 days. The accumulated
rates over the entire linear uptake phase were determined by the slope of the obtained linear regression plots between $V_{eq}$ and $T$ within 73 days, reflecting the average $R$ for the first 4 deployment intervals (without the 92-day results) (Figure 2). The sampling rates of monosaccharides were 1.1 m$^3$/d for levoglucosan (Figure 2a) and galactosan (Figure 2c), and 1.5 m$^3$/d for mannosan (Figure 2b), respectively. Due to hemicellulose being less structured compared to cellulose, hemicellulose thermal decomposition products, such as mannosan, were presumed to be more readily captured by the PUF, therefore resulting in a relatively higher sampling rate. Though the PUF-PAS sampling rates of monosaccharides are not as high as those of mainly gas-phase SVOCs including PCBs, OCPs, and PBDEs, which usually take the sampling rate range of 3-4 m$^3$/d, they are comparable with those of reported particle associated SVOCs. For example, the PUF-PAS sampling rates for monosaccharides were slightly higher than those for the particle associated PAHs detected in the southern Czech Republic (~0.7 m$^3$/d) and non-industrial indoor environments (0.2-0.9 m$^3$/d), and were comparable to the measured average rates for the PCDDs/Fs (1.4-2 m$^3$/d), which were also mainly particle-bound, detected in South Korea and Spain. Generally, the PUF-PAS sampling rate of particle-associated SVOCs were lower than those of the gaseous phase dominant SVOCs, but at the same order of magnitude for both gas-phase and particle-associated SVOCs. It has to be mentioned that these reported $R$ was derived by different passive samplers. A recent study evaluated particle infiltration efficiencies (PIEs) of PUF-PAS of several popular designs. The varied PIEs from ~54% to 103% may lead to varied particle collection efficiency of PUF-PAS in different designs. It is speculated that the larger interior volume of the sampler chamber than the air exchange capacity would probably lower the PIEs. For our current sampler, the internal volume of ~5200 cm$^3$ and the ratio of internal volume and gap surface area of ~36
are between those of LANCS and MONET samplers (Table S1), which might be one of the reasons for the low $R$.

Likewise, sampling rates are not only influenced by the physicochemical properties of the target compounds, the superficial area and the volume of the PUF, the design of sampler, but also by the atmospheric conditions and meteorological parameters, such as wind speed, temperature, humidity, and aerosol concentration.\textsuperscript{26, 38, 39} For specific compounds, sampling rates could be varied in different regions. Some previous papers mentioned high sampling rates of particle-associated polycyclic aromatic compounds (PACs) (5\textendash 8 m$^3$/d) in Canada,\textsuperscript{21, 31} and even higher sampling rates of particle-associated PAHs than those of some gaseous PAHs in a furnace area of alloy factory, an occupational environment (1.3\textendash 10 m$^3$/d).\textsuperscript{20} As mentioned above, the gas-particle equilibrium of monosaccharides might be influenced by the particle-phase liquid water.\textsuperscript{15} The air humidity in Southern China is generally higher than that of the high latitude areas and countries, might become one of the important reasons contributing to the low sampling rates of monosaccharides in this area.

Moreover, sampling rates were found as a function of wind speed.\textsuperscript{21, 26, 57} Higher wind speeds (>5 m/s) would experience non-linear aerodynamics and approach to chemical equilibrium rapidly.\textsuperscript{57} When the wind speed is higher than 4 m/s, fine particles can form clusters of larger size inside the PUF,\textsuperscript{58} which would decrease the sampling rate of particle-bound compounds.\textsuperscript{26} In this study, the wind speed was mostly lower than 3.3 m/s during the calibration study, which could be regarded as low wind speed (Table S2). Besides, with the low wind speed, wind direction changing would not greatly influence the time-weighted average (TWA) concentrations of monosaccharides in a region.

Besides the above uncertainties of sampling rates, other potential sources might also cause the propagated errors. For example, the variable air concentrations of monosaccharides might be
brought by the less well-mixed air from the accidental occurrences of fire episodes. Keeping the sampling sites far away from the BB point sources, could greatly avoid the interruption of accidental fire occurrences during the sampling campaign. Though the high temperature in summer would facilitate the evaporation of monosaccharides, the breakthrough of monosaccharides only occupied less than 3% of the total concentrations of monosaccharides tested by the 7-day continuous active sampling. The negligible breakthrough value probably due to the low concentrations of monosaccharides and good air quality during the summer of Guangzhou.

Lower $V_{eq}$ values of ~80 m$^3$ were derived for particle-phase levoglucosan over the 73-day deployment, compared to ~420 m$^3$ for gas-phase levoglucosan, suggesting that approximately 20% of the ambient particles were sampled by the PUF disk. It was higher than that of the previous estimation of 10% ambient particles sampled by PUF disk.$^{26}$ Besides, previous studies have shown that the agreements between the AAS and the PAS data for mainly particle-associated species were well within a factor of 2-3,$^{22,30,55,56}$ suggesting the PUF-PAS offers a feasible alternative to AAS when assessing the ambient concentrations of monosaccharides. Therefore, it is appropriate to apply the PUF-PAS to examine spatial patterns of monosaccharides at a regional scale.

### 3.2 Spatial Distribution of Monosaccharides

Since there were no distinct differences of the atmospheric conditions and meteorological parameters between the periods of PRD sampling campaigns and calibration exercise, (Table S2 and Table S5), and no unusual events occurred around the sampling sites during the sampling campaigns, the derived sampling rates of PUF-PAS for monosaccharides could be directly applied in the PRD region. Based on the derived sampling rate, a spatial map of monosaccharide air concentrations across the PRD is shown in Figure 3 and Table S10. In the present study, the detected concentrations
of levoglucosan (L), mannosan (M) and galactosan (G) in Jan-Apr had ranges of 28 (ZH)-200 (BL) ng/m$^3$, 3.4 (ZH)-29 (BL) ng/m$^3$, and 1.9 (ZH)-120 (BL) ng/m$^3$, with means of 91±56 ng/m$^3$ (L), 11±8.8 ng/m$^3$ (M) and 41±46 ng/m$^3$ (G), respectively. However, in Jul-Sep, concentrations decreased to the ranges of 10 (ZH)-51 (BL) ng/m$^3$ (L), 1.1 (TJ)-10 (JL) ng/m$^3$ (M), and 1.8 (ZH)-24 (JL) ng/m$^3$ (G), with average values of 23±13 ng/m$^3$ (L), 3.9±3.6 ng/m$^3$ (M) and 7.7±6.8 ng/m$^3$ (G), respectively. These results are comparable with the concentrations of monosaccharides previously detected in Guangzhou and the PRD in recent years. Likewise, lower concentrations of monosaccharides were found in summer or in dry seasons compared to those in other periods (Table S11).$^{34,59-61}$ Most of the previous studies were conducted on PM$_{2.5}$ samples, which were different from the current study of the PUF disks samples that both of the gas and particle-phases of the target compounds were collected. $^{25}$ However, these results are still of highly referable meanings, suggesting that the estimates of air concentrations derived from the PUF-PAS are reliable.

It is noteworthy that the detected concentrations of galactosan were higher than mannosan concentrations in Jan-Apr in the PRD area of present study, which is in agreement with the other studies on smoke particles derived from environmental samples $^{62}$ and source samples, such as the combustion of rice straws, biomass briquettes and grasses, $^{63}$ suggesting that agricultural waste was the primary biomass burning product. $^{62}$ Generally, concentrations of levoglucosan in the PRD were lower than those of the North China Plain $^{62,64}$ and comparable with those of western Europe (Table S11).$^8$

Among the sampling sites of the present study, the background site (TJ) had concentrations of 34 ng/m$^3$ (L), 3.6 ng/m$^3$ (M) and 4.3 ng/m$^3$ (G) in Jan-Apr and 15 ng/m$^3$ (L), 1.1 ng/m$^3$ (M) and 3.1 ng/m$^3$ (G) in Jul-Sep, which were all higher than the western North Pacific rim maritime
background in both seasons. The background concentration of levoglucosan was higher than the biannual average concentration of Atlantic maritime aerosols and high-altitude mountain background sites as well, but lower than the low-altitude coastal and continental rural sites in Europe (Table S11). As expected, the concentrations of monosaccharides in rural areas was higher than that in urban areas in this study (Table S10). The highest concentrations of monosaccharides in Jan-Apr were found at the BL site, which is located at a village bordering the city in the eastern PRD and surrounded by paddy fields and woods, followed by two suburban sites, CH and JL. The lowest concentrations were found at a coastal city (ZH) and a background site (TJ). ZH was considered a background site of the PRD region in the previous study, due to the good air quality throughout most of the year.

The ratio of levoglucosan to mannosan (L/M) has been proposed as an indicator for different types of biomass fuels, and the ratio typically ranges from 2 to 6 for softwoods but stays in a higher values, 13 to 35, for hardwoods. In this study, the ratios of L/M were found to be similar in both seasons for specific areas (Table S10). However, the values for urban areas were distinct from those of rural areas. With the exception of ZH, the L/M of urban areas had a range of 12-19, while the rural areas had a range of 2.8-7.9, with average ratios of 14±2.7 and 6.5±1.8, respectively. The results suggest that both areas were likely affected by a mixture of biomass burning emissions. Urban areas might be mainly influenced by hardwood, peat (11.4) and weed combustion (8-16), while rural areas might be possibly affected by softwood combustion and agricultural residues, such as leaves (5.5), weed, sugarcane and bamboo (5-13).

### 3.3 Relationships between Fire Activities and Concentrations of Monosaccharides derived by PUF-PAS
To evaluate the impacts of fire activities at each sampling site, a numerical model was established to count fire activities based on the MODIS data within a 50 Km radius centered on the sampling sites (Table S12). Significant correlations (n=11, p<0.01) were found between the concentrations of monosaccharides and the number of fire activities corresponding to each sampling site in Jan-Apr (Figure 4). This result further suggested that it was practical to monitor monosaccharides in air by using PUF-PAS. Besides, open BB intensity in PRD was reflected well by monosaccharide levels in Jan-Apr. However, in Jul-Sep, no significant correlation was observed between the concentrations of monosaccharides and the number of fire activities corresponding to each sampling site, which means open BB intensity was not reflected well by monosaccharide levels.

Though there was an obvious increase in fire activities noted by MODIS image, lower monosaccharides concentrations were observed by PUF-PAS in Jul-Sep than in Jan-Apr. This phenomenon is probably due to Jul-Sep meteorological conditions, excluding emission and reaction rates. In Jul-Sep, for example, warm and damp air masses from the South China Sea bring frequent precipitation and high humidity, and the strong intensity of solar radiation increases the degradation of monosaccharides during air transport before being collected by the PUF-PAS.\textsuperscript{60, 68} Moreover, high temperature induces thermal convection and the high mixing layer favors the diffusion of biomass burning, smoke and dilution.\textsuperscript{61} Thus, these major meteorological factors result in lower concentrations observed in Jul-Sep compared to other periods.\textsuperscript{60, 64} Anyhow, this phenomenon reveals that the feasibility of PUF-PAS does not have to mean that MODIS fire activities are reflected well by monosaccharide concentrations derived from PUF-PASs.

BB often occurs accidentally and in backcountry, which increases the difficulties of “capturing” fire emissions over time. With the feasibility and application of PUF-PAS monitoring
monosaccharides, TWA concentrations of monosaccharides at a regional scale are acquired. The relevant data on regional field combustion, and biomass burning information, combustion types and health assessments, would be helpful for subsequent studies on the validation of biomass burning prediction by models such as MODIS and developing fires inventories.\textsuperscript{69,70} Moreover, it provides the valuable information between biomass burning source regions and target regions via long-range transportation and migration.\textsuperscript{71}
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SUPPORTING INFORMATION

Section 1. Extraction, derivatization and GC-MS analysis

Section 2. Concentrations of Monosaccharides in the AAS Samples

Section 3. Tables and Figures

(Table S1) Information of the sampler used in the current study and comparison with three commonly used PUF-PASs. (Table S2) Basic environmental and meteorological parameters during the calibration exercise. (Table S3) Sampling date and mass of monosaccharides collected by PUF-PAS. (Table S4) Information of the sampling sites in the PRD region. (Table S5) Basic environmental and meteorological parameters during the sampling campaigns in the PRD region. (Table S6) Concentrations of monosaccharides from the AAS measurement. (Table S7) Particle-phase fraction parameter ($\phi_p$) and the ratio of gas- to particle-phase for monosaccharides. (Table S8) Correlations between monosaccharides and basic environmental parameters. (Table S9) Calculation results of equivalent air volume and accumulated sampling rates. (Table S10) Concentrations of
monosaccharides in the PRD region. (Table S11) Concentrations of monosaccharides in the references; (Table S12) Amount of fire activities within a 50 km radius centered on the sampling sites. (Figure S1) Recoveries of spiked $^{13}$C$_6$ levoglucosan in PUF disks over the 92-day deployment. (Figure S2) Accumulated amounts of monosaccharides in the PUF-PAS over the 92-day deployment. (Figure S3) Total concentrations and gas- and particle-phase concentrations of monosaccharides derived by active sampling. (Figure S4) Variations in monosaccharides, the particle-phase fraction parameter ($\phi_p$), organic matter (OM), total suspended particulates (TSP) and relative humidity (RH) during the calibration exercise. (Figure S5) Correlations between daily air concentrations derived by active sampling and daily accumulated amounts derived by PUF-PAS during each period.

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Captions

Figure 1. Map of the sampling sites.

Figure 2. Equivalent air volume sampled for monosaccharides using PUF disks over the 92-day deployment.

Figure 3. Spatial and seasonal distribution of monosaccharides in the Pearl River Delta.

Figure 4. Correlations between fire activities and concentrations of monosaccharides in Jan-Apr of Pearl River Delta.
Figure 1
Figure 2

**Levoglucosan**

\[ y = 1.1x \]
\[ R^2 = 0.65 \]

**Mannosan**

\[ y = 1.5x \]
\[ R^2 = 0.98 \]

**Galactosan**

\[ y = 1.1x \]
\[ R^2 = 0.97 \]
**Figure 4**

- **Levoglucosan**
  
  \[ y = 8.7x + 47 \]
  
  \[ R^2 = 0.74 \]

- **Mannosan**
  
  \[ y = 1.32x + 4.5 \]
  
  \[ R^2 = 0.68 \]

- **Galactosan**
  
  \[ y = 6.12x + 9.8 \]
  
  \[ R^2 = 0.55 \]