Seasonal Variation of Saccharides and Furfural in Atmospheric Aerosols at a Semi-Urban Site

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ABSTRACT

Seasonal variability of daily particle mass and saccharides and furfural concentrations in atmospheric particulate matter in both coarse aerosols (diameter > 2.4 µm) and fine aerosols (diameter < 2.4 µm) was determined for a semi-urban area in the United Kingdom. Saccharides, which include levoglucosan, and furfural are derived from biomass burning and contribute to aerosol composition. This study examined the potential of saccharides and furfural as tracers for biomass combustion. High saccharide concentrations were observed in the autumn, but they did not show a high correlation with potassium expected in biomass smoke. These results may imply that the high saccharide concentrations are derived not only from biomass burning sources, but also from non-combustion sources, such as leaf decay. Significant seasonal variations were observed for saccharides and furfural species in fine atmospheric aerosols. Furfural is likely to be oxidized quickly in comparison with saccharides, so while saccharides such as levoglucosan are known to be fairly stable in the atmosphere, furfural could be transformed. Trajectory and factor analysis suggest that the saccharides may result from long-range transport, while furfural may be more influenced by the local sources possibly because of its shorter lifetime. This result may suggest it could give clues as to the age of biomass smoke.

Keywords: Particulate matter; Biomass smoke markers; Age of biomass smoke.

INTRODUCTION

Saccharides are among the most important water-soluble organic compounds in atmospheric aerosols which are found across urban (Medeiros et al., 2006; Jia et al., 2010), forest and mountain (Graham et al., 2003; Yttri et al., 2007; Fu et al., 2008), marine (Simoneit et al., 2004a; Wang et al., 2009; Fu et al., 2011; Zhang et al., 2012; Chen et al., 2013) and polar regions (Fu et al., 2009). They represent up to 75% of vascular plant tissues as polysaccharides (not always soluble) such as cellulose, hemicelluloses and pectin. The saccharides associated with aerosols belong to three main groups: primary saccharides (mono and disaccharides), saccharide polyols (reduced sugars) and anhydrosaccharides, derived mainly as levoglucosan (Simoneit et al., 2004a; Ma et al., 2009). As major products of photosynthesized carbon in ecosystems, saccharides have been proposed as potential markers in understanding sources, processes and transport of the important organic components in the environment (Medeiros and Simoneit, 2007).

Biomass burning is the important source of trace substances in atmosphere, which undergo subsequent reactions in the atmosphere (Simoneit, 1999). Various studies have found saccharides present in atmospheric particles from smoke plumes (e.g., Sillanpää et al., 2005), with levoglucosan (1, 6-anhydro-β-D-glucopyranose) a primary thermal degradation product from biomass burning (Simoneit et al., 1999; Medeiros et al., 2006). This compound is a major tracer of smoke from biomass fires (Simoneit et al., 2004b; Schkolnik et al., 2005) due to its atmospheric stability (Fraser and Lakshmanan, 2000). Levoglucosan is often the most dominant sugar component in fine particles and can contribute to more than 90% of the total sugar mass in tropical areas impacted by wood smoke (Simoneit, 2002). Recent studies (Hennigan et al., 2010; Hoffmann et al., 2010) have suggested that levoglucosan is prone to degradation by OH radicals in the atmosphere. Thus, its concentration during long-range transport may be lower than expected, especially in summer (Mochida et al., 2010).

Furfural is another reaction product of wood combustion, derived from pyrolysis of polysaccharides in the cellulose and hemicellulose of biomass (Edye and Richards, 1991; McKenzie et al., 1995). During combustion, high emission rates of furfural have been reported in laboratory-based...
studies (Andreae and Merlet, 2001; Ciccioli et al., 2001). In a recent study, furfural was selected to be marker volatile compounds for early fire warning systems because it is emitted at high rates prior to ignition (Paczkowski et al., 2013). However, furfural concentrations are found to be low in the atmosphere aerosols downwind from wood combustion (Simoneit, 2002) and the few furfural measurements are available for air masses derived from biomass combustion. Assuming of furfural is readily produced during combustion its relative absence in smoke plumes suggests it might be rapidly removed or degraded as the air mass ages. Saccharides and furfural have different properties in terms of their volatility, solubility, Henry’s law constant and degradation processes. Furfural can be readily removed from the atmosphere by chemical reaction and physical transformation processes (Ciccioli and Mannozzi, 2007). Although both saccharides and furfural are expected from biomass burning and contribute to aerosol composition (Olsson, 2006) the rapid transformation of furfural could lead to a decrease in the furfural saccharide ratio. Thus, the ratio and correlation between a biomass burning tracer (potassium) and furfural and saccharides in atmospheric aerosols could be a potential indicator of plume age. Only when most of the potassium is from biomass burning, can it be used as an appropriate biomass burning indicator. However, there are important limitations of potassium in the use of the marker, because potassium also has many sources, such as biomass burning, coal/charcoal burning, soil dust, fertilizers, and even traffic exhaust emissions in small amounts (Andreae and Merlet, 2001; Urban et al., 2012). Seasonal variations in the particulate matter mass and chemical composition depend on factors such as emission/transformation rates, distance from the source, physical conditions of the medium where they are introduced (Perrino et al., 2010; Singh et al., 2012; Ni et al., 2013; Saitanis et al., 2013) and meteorological conditions (e.g., mixing depth of the atmosphere, rainfall, wind speed and prevailing wind direction). Soil and vegetation particles are mostly re-suspended during summers, secondary pollutants, produced by precursor reactions in the atmosphere, rapidly increase during periods of atmospheric stability, and domestic heating during cold periods (Perrino et al., 2013). In this paper, we present the results of fine and coarse particle mass, saccharides and furfural concentrations in atmospheric aerosols at the semi-urban background site in UK. Additionally, as this is the first study investigating saccharides and furfural concentrations in over all the seasons, the seasonal variation will hint at their possible sources leading to the potential indications of smoke age.

METHODS

Site Description
Ambient particulate matter samples were collected at University of East Anglia (UEA) located in Norfolk in the United Kingdom, 52.62°N and 1.24°E. The measurements were conducted from 10 June 2007 to 5 March 2008. The UEA site is on the western edge of the city of Norwich about five kilometers from the city centre. It is the regional administrative centre and county town of Norfolk. The site represents a semi-urban area of England. The urban area of Norwich has a population of 259,100. The county (Norfolk - 5370 km²) is largely rural with a low population density. The British Isles, experiences a temperate maritime climate with the mean annual temperature over the region varying from just over 9°C to around 10.5°C. Averaged across the year, the prevailing wind direction is from the south-west. The main local anthropogenic particle emission sources affecting the particle concentrations are power generation, traffic and during winter season domestic fuel combustion.

Aerosol Sampling
The particulate matter was collected on the roof of the academic building (10 m from the ground). Individual samples were collected over 24 hour periods. The samples were collected during three different seasons from June 2007 through March 2008. Meteorological conditions were recorded for the summer (10 June–20 August 2007), autumn (10 September–10 November) and winter (15 December 2007–5 March 2008) sampling campaigns. Samples were collected using an Andersen (model GS2310) sampler at flow rate of 1 m³/min. For collection of size distributed aerosols, the sampler used a multi-stage cascade impactor. Six stages segregated the size diameters of atmospheric aerosols. However, this study used only stages 2 and 3 of 6 stages of the impactor to collect coarse mode aerosols (diameter size more than 2.4 µm) and a backup stage was used to represent fine mode aerosols (diameter size below 2.4 µm). The samples were collected on binder-free, high-grade borosilicate glass microfiber filter papers (heated at 550°C for 4 h). The coarse mode aerosol sampling from stages 2 and 3 used 5.63 × 5.38 inch slotted glass fibre filter paper (Westech Instrument) in each plate. A glass filter paper, 8 × 10 inch, was used as a backup filter paper to collect fine mode aerosols. The field blanks are collected by placing the sampling media in the sampler and removing without sampling. A minimum of one blank was collected each season.

After sampling, the filters were carefully packed in aluminum foils, conditioned in desiccators for 24 h prior to weighing and stored in a refrigerator (4°C) until analysis. Sections of the filter papers with particulate samples were cut into 1 cm² squares, and put into a new disposable centrifuge tube and 40 mL of ultra pure water (Neptune Analytical 18.2 MΩcm resistivity) was added. The mixture was sonicated for 40 minutes and passed through a syringe filter with a pore size of 0.45 µm. The mixed solution was diluted to 100 mL in a volumetric flask and kept at 4°C until analysis.

Chemical Analysis
For saccharide analysis, the sample solution (5 mL) and 10 mL of the anthrone-sulfuric solution (anthrone 2.0 g was mixed in 1 L of sulfuric acid, 95%) was added to a 25 mL volumetric flask. The solution was mixed by swirling, allowed to stand for 10 minutes then boiled 10 minutes until the reaction was completed. After this mixed solution was cooled, it was ready to use for measurement. The absorbance was measured with an ultra violet-visible
polyols and their derivatives, saccharide polymers such as
this study would include monosaccharides and disaccharides,
CHN analyser. A 17 mm × 2 punch from the filter paper was
performed with suppressed conductivity detection. The
cations were separated by CS16 3 × 250 mm using a methanesulfonic
anions with a potassium hydroxide eluent. The cations
(sulphate, nitrate and chloride) were measured in the same
magnesium, potassium and calcium) and three anions
the blank samples.

The limit of detection was estimated by standard
deviation of the blank solutions. The detection limit of this
method was 7.0 µmol/L, calculated using the mean and
standard from the blank samples. The calibration curve
was established by using levoglucosan solutions at the
different concentrations and treated with the same procedure
as in the determination of saccharides in the collected
samples. The anthrone method as used by Morris (1948),
Laurentin and Edwards (2003), Fartas et al. (2009), Latif
et al. (2011, 2012) and Scaramboni et al. (2015) was
adopted in this work. In the first reaction step, glucose was
dehydrated by sulfuric acid, leading to the formation of
hydroxymethylfurfuraldehyde. This product condenses with
anthrone forming 10-[(5-hydroxymethylfuranyl)methylene]-
anthrone which makes the solution turn from yellow to
green (Asquieri et al., 2013). The saccharides measured in
this study would include monosaccharides and disaccharides,
polysols and their derivatives, saccharide polymers such as
dextran, glycojen, cellulose, and starch, several amino acids
and polysaccharides (Morris, 1948; Scaramboni et al., 2015).

Furfural analysis took the sample solution (3 mL), 15 mL
of p-toluidine solution (p-toluidine 10.0 g mixed with 10.0
mL glacial acetic acid then made up to 100 mL with 2-
propanol) and 3 mL of barbituric acid solution (barbituric
0.5 g mixed with 100 mL of Milli Q water) finally diluted
to 25 mL with distilled water. Samples were kept at 18°C
for 5 minutes after which the absorbance was immediately
measured with ultra violet-visible spectrometer at wavelength
585 nm. These procedures were completed in 1–2 minutes
(Akkan et al., 2001). The limit of detection for furfural was
estimated by standard deviation of the blank solutions as
0.1 µmol/L, calculated using the mean and standard from
the blank samples.

The major ions, including four cations (sodium, magnesium, potassium and calcium) and three anions
(sulphate, nitrate and chloride) were measured in the same
extract as above using a Dionex DX600 ion chromatograph.
An Ion Pac AS18 2 × 250 mm column was used to separate
anions with a potassium hydroxide eluent. The cations
were separated by CS16 3 × 250 mm using a methanesulfonic
acid (MSA) eluent. The Dionex chromatography was
performed with suppressed conductivity detection. The
carbon and nitrogen contents were measured by a CE440-
CHN analyser. A 17 mm² punch from the filter paper was
analysed with acetanilide as the standard, while filter papers
without particulate matter were also analysed as blanks.

Backward Trajectories and Principle Component Analysis

Identification of the source regions for air masses was
investigated using backward trajectories using NOAA
HYSSPLIT v 9.4 model (Rolph, 2003; Draxler and Rolph,
2011). In this study, 72-hour-air mass trajectories ending at
the sampling station were calculated with the online version
of the model as a tool to determine potential backward
trajectories that air crossed sampling areas at 100, 500 and
1000 meters above ground level. These model runs assimilated
all available observations to produce dynamically consistent
6-hourly analyses and the Global Data Assimilation System
(GDAS) meteorological archive data were chosen as the
input data. The backward trajectories were computed at
1200 UTC for each sampling day.

Source apportionment based upon chemical speciation
used principal component analysis, PCA. Contributions of
saccharides and furfural to atmospheric aerosols in this
study were analyzed for both fine mode and coarse mode
aerosols collected at UEA. PCA was applied using a varimax
normalization. The eigenvalues were used to determine the
number of factors along with the variance in each factor
after rotation (Park and Kim, 2005). The identification of
the contribution to factors was attempted by examining the
factor loadings of the aerosol trace elements.

RESULTS AND DISCUSSION

Particulate Matter Concentration

The concentrations of particles, saccharides, furfural and
correlation of saccharides with furfural are summarized in
Table 1. The concentration of particles shows the dominance
of the fine mode. The seasonal average aerosol concentration
in fine mode aerosols ranged between 12.4–19.5 µg/m³, while
the concentration in coarse mode aerosols ranged between
7.2–10.4 µg/m³. The fine mode aerosol concentrations were
about two times higher than coarse mode aerosols. The
highest abundance of aerosols was detected in the winter
and t-tests showed that the fine mode winter concentrations
were significantly different from autumn and summer
(both p = 0.03). In the coarse mode, summer is significantly
different from the autumn and winter with p = 0.02 and
0.005, respectively.

Saccharides and Furfural Concentration

The comparisons of saccharide and furfural concentrations
between seasons were analysed with a range of statistical
tools. Analysis of variance (ANOVA) with Bonferroni test
and t-test analysis was used for normally distributed data,
and data which were not normally distributed were analyzed
by the Chi-square test. The concentrations of saccharides
present in the atmospheric aerosols were consistently higher
as fine mode aerosols than coarse mode aerosols. The average
concentration of saccharides over the different seasons was
956.6–2983.4 ng/m³ (5.9–18.4 nmol/m³) as fine mode
aerosols and 227.0–908.0 ng/m³ (1.4–5.6 nmol/m³) as coarse
mode aerosols (Figs. 1(a) and 1(b)). It should be noted that the
ng/m³ unit is only an estimate, which assumes all saccharide
is present as levoglucosan.

The highest percentages of saccharides in the fine mode
were found in autumn, followed by summer and winter,
respectively. Statistical tests showed that the concentrations
of saccharides in both coarse and fine mode in autumn were
significantly different (p < 0.05) from other seasons. These
results indicate that the saccharide concentrations increased
dramatically in autumn atmosphere. The concentrations of
saccharides were not expected to correlate with aerosol
loading in Norwich, because most of particles seemed likely
to derive from urban sources such as vehicles. However,
both fine and coarse mode show a modest correlation with
the aerosol concentrations in winter (both r = 0.7, p < 0.05).
Table 1. Concentrations of particles, saccharides (S) and furfural (F).

<table>
<thead>
<tr>
<th>Season</th>
<th>Mode</th>
<th>Particles</th>
<th>Saccharides</th>
<th>Furfural</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine</td>
<td>µg/m³</td>
<td>ng/m³</td>
<td>µg/m³</td>
</tr>
<tr>
<td>Summer</td>
<td>25</td>
<td>12.4</td>
<td>38.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Coarse</td>
<td>7.2</td>
<td>38.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Autumn</td>
<td>24</td>
<td>12.6</td>
<td>86.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Winter</td>
<td>18</td>
<td>8.5</td>
<td>48.0</td>
<td>0.2</td>
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Values are means. Numbers in parentheses are standard derivations.

This result suggests that domestic wood-burning in houses in winter might contribute to the saccharide concentrations. In other seasons there is only weak correlation \( (r = 0.1–0.4, p > 0.05) \). Furthermore, the saccharides were found to range 5.4–23.7% of fine mode aerosols and 3.2–10.7% of coarse mode aerosols. Previous studies in China found that the concentration of saccharides was highest in the fall, 326.0–725.6 ng/m³ \((0.1–0.2\% \text{ of TSP})\), which is similar to the trend in agricultural activities \( (Bi et al., 2008; Ma et al., 2009) \). There is a similar trend which suggests that saccharides in fine mode aerosols were higher than those of coarse mode aerosols, Engling et al., 2006 also found that the majority of the anhydrosaccharides (levoglucosan) mass sampled during chamber and stack burn experiments was observed in fine particles \((\text{diameter} < 2.5 \mu\text{m})\), and also the fraction measured in coarse particles \((\text{diameter} > 2.5 \mu\text{m})\) was approximately 1.2% of the fine particles.

The highest furfural concentration at the UEA site was observed in fine mode aerosols. Peak concentrations were detected in autumn, with 153.7 ng/m³ \((1.6 \text{ mmol/m}^3)\) in fine mode and 86.5 ng/m³ \((0.9 \text{ mmol/m}^3)\) in coarse mode aerosols, as shown in Figs. 1(c) and 1(d). The average percentage of furfural in total particle mass found to be high in autumn. Furthermore, the amount of furfural found as fine mode aerosols was approximately 0.1–0.6% of the total mass of fine particles. The seasonal distributions of furfural concentrations in the atmosphere were found to be different, with the highest levels in autumn followed by summer and winter, respectively. Moreover, a statistical test showed that the airborne concentrations of furfural in autumn were significantly higher \((p < 0.05)\) than those from of other seasons. In winter furfural had a relatively low abundance in the aerosol because the furfural concentrations in particles may be diluted by the larger aerosol mass. However, furfural in fine mode aerosols shows a weak correlation with the aerosol concentrations in winter \((r = 0.27)\) while the other seasons did not show any correlation. Overall, the concentrations of saccharides were higher than those of furfural. The peaks of saccharide and furfural concentrations were observed in autumn and significantly different \((p < 0.05)\) from those of the coarse mode aerosols and from other seasons. This indicates that those substances are not a simple function of particle mass, and thus their relative concentration in the particles varies.

This work is the first study of seasonal of saccharides and furfural in atmospheric aerosols. However, a few other studies have reported seasonal measurements of saccharides \( (Ma et al., 2009; Mochida et al., 2010; Chen et al., 2013) \). Saccharides, as levoglucosan and additionally furfural, are pyrogenic species and markers of biomass burning and emitted in various types of biomass burning. Emission factors for furfural from savanna forest and grassland, tropical forest and also extratropical forest fires are 230, 370 and 460 mg/kg burned, respectively. The emission factors of levoglucosan are 280, 420 and 750 mg/kg burned, respectively \( (Andreae and Merlet, 2001; Lemieux et al., 2004) \). Although, high emission rates of furfural and levoglucosan have been reported from laboratory based biomass combustion, furfural is found to be at low concentrations in the atmospheric
particles emitted during biomass burning (Simoneit, 2002; Ciccioli and Mannozzi, 2007). By assuming the emission rates to be correct, it might be that furfural had been missing from particles (i.e., degassing or oxidation) or failure to transfer to the particles. Low concentrations could also suggest that saccharides and furfural have different properties such as volatility and degradation processes. In previous studies, saccharides such as levoglucosan produced during biomass burning have been found in aerosols that have travelled long distances, showing its stability during long-range transport. Moreover, these studies illustrate the potential of levoglucosan, which is resistant to degradation in the atmosphere as a biomass tracer (Simoneit et al., 1999; Fraser and Lakshmanan, 2000; Poore, 2002; Simoneit et al., 2004a; Simpson et al., 2004; Medeiros et al., 2006; Robinson et al., 2006; Mochida et al., 2010; Chen et al., 2013).

**Correlation between Saccharides and Furfural and Potassium**

Saccharides and furfural were found in the atmosphere at UEA. The weak but significant relationship ($r = 0.24-0.38$, $p < 0.05$) shows saccharides correlated with furfural in fine mode aerosols suggesting that they were emitted from a similar source, probably biomass burning. This is supported by Simoneit (2002) who reported that a saccharide such as levoglucosan is found in the fine particles from wood smoke. Conversely, the saccharides and furfural concentrations in coarse mode aerosols did not show any correlation ($r = 0.02-0.1$). It suggests that the coarse mode saccharides are likely to be dispersed from the ecosystem. However, it is clear that higher airborne concentration of furfural and saccharides were found in autumn and also these concentrations may be the result, in particular, of the smaller mixing depth. Additionally, sugar production in the ecosystem also can be a source of saccharides in the autumn, and greater contribution of metabolites from microbial degradation of primary saccharides during early autumn, and the period of leaf senescence and decay (Medeiros et al., 2006). Based on very limited data, the relationship between ambient saccharide and furfural concentrations depend on emissions of material burned may vary from source to source, and exhibit significant variations with biomass properties. This high degree of variation is likely due to a combination of factors, including fuel composition, fuel heating value, bulk density, oxygen transport and combustion conditions (Lemieux et al., 2004; Evtyugina et al., 2013).

Correlations between saccharides and non-sea-salt potassium (NSS K+) were found in both coarse and fine mode aerosols during the winter (Figs. 2(a) and 2(b)), which supports combustion and heating as a source of saccharides. In contrast, saccharides although found to be at highest concentrations in the autumn, they did not show a strong correlation with potassium. These results may imply that the high saccharide concentrations derive not only from
biomass burning sources, but also from non biomass burning sources, such leaf decay in the fall (Medeiros et al., 2006). An alternate possibility might be that they arise because the types of biomass burnt during the autumn differ from that of the winter. Biomass burning in the autumn emitted high levels of saccharides, but different levels of potassium whereas stronger correlations of concentration of saccharides and potassium were produced in the winter. As mentioned above in the discussion of biomass burning sources, different composition of the biomass such as straw and foliar material produce different chemical emission patterns (Sheesley et al., 2003; Ward et al., 2006; Iinuma et al., 2007). Similarly, Sullivan et al. (2008) reported that dust and needle burning emit very little water-soluble potassium, but varying amounts of levoglucosan, while the high correlations between levoglucosan and potassium were found in branch ($R^2 = 0.79$) and straw burning ($R^2 = 0.62$).

Average ratios of potassium and saccharides in the particles collected at UEA are shown in Table 1. The average K/saccharides ratios in coarse mode aerosols were found to be higher than those in fine mode aerosols during summer, autumn and winter. The highest ratios of K/saccharides were found in summer, as 0.64 in coarse mode. The ratios of 0.27 and 0.17 were found in the winter followed by the ratios of 0.16 and 0.07 in the autumn, respectively. In this study, we quantified saccharides which may include other sugar species such as levoglucosan, and investigated the relationship between saccharides and potassium in term of K/saccharide ratios. However, Caseiro et al. (2009) reported K/levoglucosan ratios in the Austrian autumn and summer ranging from 2 to 4.5 and from 0.6 to 1.1 in the winter. Similarly, Cheng et al. (2013) also reported that the levoglucosan/K ratio was lower during a typical summer period ($0.21 \pm 0.16$) compared with a typical winter period ($0.51 \pm 0.15$) and concluded that levoglucosan/K ratios are capable of distinguishing emissions from the burning of crop residues. Previous studies have used the relationship between levoglucosan and potassium to ascribe the sources such as coniferous and deciduous woods or differences between smouldering and flaming combustion. Schmidl et al. (2008) reported K/levoglucosan ratios ranging between $0.005–0.019$ and $0.031–0.05$ for Austrian softwoods and hardwoods, respectively. Viana et al. (2008) reported K/levoglucosan in the range $0.003-0.004$ for rice straw burning in Spain. In studies of burning North American wood types in fireplaces, K/levoglucosan ratios were in the range $0.017–0.23$ (Fine et al., 2001, 2002). In contrast to those low K/levoglucosan ratios from sources such as fireplaces and stoves, higher ratios of K/levoglucosan were reported in agricultural and forest fire studies. Hay et al. (2005) found K/levoglucosan of 7.4 in wheat straw burning and Pio et al. (2008) presented K/levoglucosan in the range 1.8–8.7 for summer forest fires in Portugal while Ward et al. (2006) and Fine et al.
(2001) observed lower ratios, reporting K/levoglucosan ratios of 0.11 and 0.05 for forest fires and fireplace combustion, respectively.

Correlations between furfural and NSS K⁺ were found in fine mode aerosols, with the highest correlation found in the winter (Fig. 2(c)). This result may be because furfural in fine mode aerosols is related with emissions such as potassium, as a tracer of biomass combustion. As with the saccharides, high concentrations of furfural were found in the autumn, but did not show a correlation with potassium. This result may be because the types of biomass burning during the autumn emit high furfural, but varying levels of potassium and may also be related with their lifetimes, transport from biomass burning sources and the quantities existing in the atmosphere. The average ratios of potassium and furfural are shown in Table 1. The highest ratio was found in the winter in both fine and coarse mode aerosols. The average K/furfural ratios ranged from 1.05 to 6.29 in fine mode aerosols and from 1.27 to 14.23 in coarse mode aerosols.

This study found the ratios of K/furfural were higher than those of K/saccharides due to the lower concentrations of furfural found in the UEA samples. Although saccharides and furfural are tracers from biomass burning (Edye and Richards, 1991), furfural was detected at low concentration. These results support the view that furfural had disappeared from particles, while saccharides are known to be more stable in the atmosphere (Fraser and Lakshmanan, 2000), and they may also suggest that saccharides and furfural have different properties such as volatility and degradation processes.

**Possible Sources of Saccharides and Furfural in Atmospheric Aerosol**

Trajectory analysis was used to identify sectors for saccharide and furfural sources collected at the UEA site. The atmospheric samples at UEA were affected by air mass trajectories from UK land (45 of 67, i.e., 67%) more than European (25%) and marine sectors (8%). Example plots of trajectories from UK, Europe and marine sectors to the UEA sampling station are in supplementary materials (Fig. S1). Trajectory analysis showed air mass trajectories from the European sector demonstrate median concentrations of saccharides higher than those of the UK land and marine sectors as in Fig. 3(a). On the other hand, the UK land sector showed high median concentrations of furfural (Fig. 3(b)). Although the differences in these median concentrations were not statistically significant, they hint that saccharide concentrations may result from long-range transport, while furfural concentrations may be more influenced by the local sources due to the short lifetime of furfural. However, more data is required to confirm this supposition. These may suggest that the concentrations of saccharides and furfural from Europe were influenced by biomass burning activities of continental countries such as agricultural burning, domestic burning and forest fires.

Source contributions of fine and coarse mode aerosols were identified by the principal component analysis (PCA) with varimax rotation as presented in Table 2. Results of the PCA revealed three factors in fine mode aerosols, accounting for more than 76% percent of the variance. Factor 1 has high loadings for Cl⁻, SO₄²⁻, NO₃⁻, K⁺, total carbon and total nitrogen, accounting for 46.4% of the total variance. The origin of this group is not clear, but the spread of the points is interpreted as showing changes of these species in summer, autumn and winter (Fig. 4(a)). Trends of the scores indicate an increase during the winter, especially notable is a group with high scores found in winter. Factor 2 contains high loadings for Mg²⁺, Na⁺ and Ca²⁺ which accounts for 16.5% of the total variance and mainly links typical crustal elements. These earth mineral elements suggested that this component might be identified as a crustal group. The score plot of Factor 2 is shown in Fig. 4(b). The overall spread of the points fluctuated during the seasons showing no obvious pattern. The crustal group may derive from man-made or natural sources in Norwich area and Europe.

Factor 3 accounts 13.4% of the total variance with high loadings for saccharides and furfural. As saccharides and furfural are biomass tracers, this result may hint that Factor 3 has a biomass burning emission component. Moreover, this result can support the view that biomass burning sources contributed in the autumn, as demonstrated in the trajectory analysis. Possible sources could be the bio-fuel power stations around the Norwich area and agricultural burning. The score plot is shown in Fig. 4(c). The scores for saccharides and furfural were found to be high in the autumn.

For the coarse mode aerosol, four factors account for more than 83% percent of the variance. Factor 1 has high loadings for Cl⁻, Na⁺ and Mg²⁺ accounting for 41.2% of the total variance and links to sea salt aerosols. Regarding the high loadings of these marine components, it shows that the coarse mode aerosols collected at UEA were influenced by marine sources. Factor 2 accounts for 17.1% of the total variance containing high loadings for SO₄²⁻, K⁺ and Ca²⁺. The contribution of this group is not clear and may not be easily explained as originating from the same source. This component represents anthropogenic emissions (SO₄²⁻ and K⁺) i.e., fossil fuel and fertilizer as well as soil-dust (Ca²⁺). The contribution of Factor 3 is also not clear, but in coarse mode aerosols it explains 13.1% of the total variance and has high loadings for saccharides and NO₃⁻. The source of NO₃⁻ is interpreted as perhaps the combination of a variety of anthropogenic emissions. Saccharides, most likely derived from leaf decay in the autumn. Factor 4 accounts 11.7% of the total variance with high loadings for furfural. The score plot is shown in Fig. 4(d). A high score was found in late summer through autumn. This result identifies the source of Factor 4 as combustion emission since furfural is a combustion tracer from biomass burning and automobile combustion and here possible sources are biomass burning in the area around Norwich.

**CONCLUSIONS**

This study shows that significant seasonal variations of saccharides and furfural occurred in the mass concentration and chemical composition of atmospheric particles in the semi urban area, Norwich, UK. These variations mainly
arose from atmospheric mixing and changes in the source experienced in this region. These saccharides and furfural could be are potential tracers of the age of the aerosols in biomass smoke. The concentrations of saccharides were higher than furfural concentrations in all samples. It was likely that furfural was ineffectively transferred to particles or oxidized quite rapidly, while saccharides such as levoglucosan are known to be more stable in the atmosphere.

Fig. 3. Sources of saccharides and furfural based on trajectory analysis. The first quartile (Q1 or 25th percentile) is the median of the lower half of the data set. The third quartile (Q3 or 75th percentile) is the median of the upper half of the data set.

Table 2. Results of principle component analysis.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fine mode aerosols</th>
<th>Coarse mode aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Factor 1</td>
<td>Factor 2</td>
</tr>
<tr>
<td>Saccharides</td>
<td>0.30</td>
<td>0.17</td>
</tr>
<tr>
<td>Furfural</td>
<td>−0.15</td>
<td>−0.78</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.83</td>
<td>−0.11</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.65</td>
<td>0.27</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.85</td>
<td>0.33</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.28</td>
<td>0.66</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.77</td>
<td>0.19</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.42</td>
<td>0.74</td>
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<tr>
<td>Calcium</td>
<td>0.16</td>
<td>0.91</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.91</td>
<td>0.21</td>
</tr>
<tr>
<td>% of Variance</td>
<td>5.10</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>46.38</td>
<td>16.50</td>
</tr>
</tbody>
</table>

Note: The analysis of the data was performed by SPSS 16.0 Only factor loading values with moduli larger than 0.1 are presented and the factor loading values with moduli higher than 0.5 are in bold.
The current study supports the view that saccharides can be found at high concentration even far away from their sources, while furfural had higher concentrations when it close to sources.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


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**Fig. S1.** Example of trajectories. Result of the HYSPLIT model 3-day backward trajectory analysis started at 1200UTC, at altitudes of 100, 500 and 1000 m at UEA station. The top and bottom panels display horizontal and vertical motion. Symbols denote the location of the air parcel every 6 hours.