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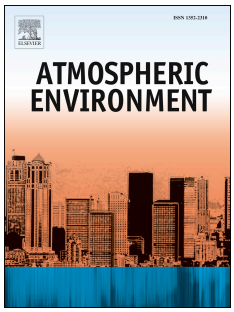

Evaluation of biomass burning across North West Europe and its impact on air quality

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Evaluation of Biomass Burning across North West Europe and Its Impact on Air Quality

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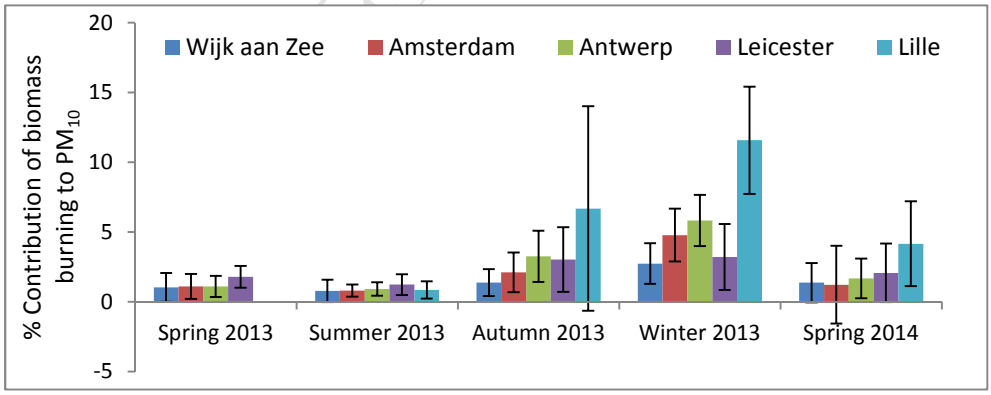
Graphical Abstract



Abstract

Atmospheric particulate pollution is a significant problem across the EU and there is concern that there may be an increasing contribution from biomass burning, driven by rising fuel prices and an increased interest in the use of renewable energy sources. This study was carried out to assess current levels of biomass burning and their contribution to total PM_{10} across five sites in North-West Europe; an area which is frequently affected by poor air quality. Biomass burning was quantified by the determination of levoglucosan concentrations from PM_{10} aerosol filters collected over a 14 month period in 2013/2014 and continued for a further 12 months at the UK site in Leicester. Levoglucosan levels indicated a distinct period of increased biomass combustion between November and March. Within this period monthly average concentrations ranged between 23±9.7 and 283±163 ng/m^3, with Lille showing consistently higher levels than the sites in Belgium, the Netherlands and the UK. The estimated contribution to PM_{10} was, as expected, highest in the winter season where the season average percentage contribution was lowest in Wijk aan Zee at 2.7±1.4 % and again highest in Lille at 11.6±3.8 %, with a PM_{10} mass concentration from biomass that ranged from 0.56 µg/m^3 in Leicester to 2.08 µg/m^3 in Lille. Overall there was poor correlation between the levoglucosan concentrations measured at the different sites indicating that normally biomass burning would only affect atmospheric particulate pollution in the local area; however, there was evidence that extreme burning events such as the Easter fires traditionally held in parts of North-West Europe can have far wider ranging effects on air quality. Network validation measurements were also taken using a mobile monitoring station which visited the fixed sites to carry out concurrent collections of aerosol filters; the result of which demonstrated the reliability of both PM_{10} and levoglucosan measurements.

Keywords: Levoglucosan, monosaccharide anhydrides, biomass burning, North-West Europe, PM_{10}

Introduction

Exposure to atmospheric particulate matter (PM) has been shown to have detrimental effects on health, in particular in vulnerable groups such as the elderly, children and those with pulmonary or cardiovascular disease [1-3]. There are a variety of anthropogenic activities which contribute to total PM_{10} including energy production, transport, agriculture and industry; emissions from many of which have decreased over the last 20 years [4]. There is, however, increasing concern regarding the increasing contribution of biomass burning to total PM_{10}. Air pollution from biomass burning in some regions of Europe, such as in Scandinavia and Alpine areas, has for a long time been considered a significant contributor to atmospheric PM [5]. In some alpine areas in Europe, where wood burning is the predominant domestic heat source, biomass smoke can comprise more than 50% of the organic PM produced in the winter season [6]. More recently, evidence is emerging suggesting that this problem is no longer limited to these areas and that biomass burning is becoming an increasingly widespread problem across the whole of Europe [6-10].

There are several factors which are likely to be contributing to this ongoing increase in biomass combustion. One large driving force is the effort of the European Union to reduce its use of fossil fuels and increase the use of renewable energy, which is driving a return to biomass burning [5]. Current EU forecasts are anticipating a 57–110% increase in biomass burning between 2010 and 2020 [11]. Other schemes on a national level have similar aims; for example in the UK the Department for Energy and Climate Change has developed the world's first long-term financial support programme for renewable heat, known as the Renewable Heat Incentive [12]. The scheme pays participants who generate and use renewable energy to heat their buildings. Finally, the increasing costs of traditional fuel sources are also having an effect: for example in Denmark increasing fossil fuel costs have contributed to a doubling in the number of wood stoves and boilers over a ten year period [13].

The ability to quantify the contribution of biomass burning to total atmospheric PM is, therefore, becoming increasingly important for air quality management. Although several markers of biomass burning have been applied for this purpose previously, the cellulose-specific monosaccharide anhydride, levoglucosan, is often considered the marker of choice. Levoglucosan has several advantages as a biomass burning marker: it is emitted in relatively large quantities, improving the consistency of its measurement; it is subject to little interference from other sources; it has relatively high stability in the atmosphere [6, 14] and its reliability has already been demonstrated previously in several studies [15-17]. Examining the ratios of levoglucosan to its isomers can also give further valuable information for the source identification of the specific type of biomass burnt. The combustion of lignite, for example, has been shown to produce either very low or undetectable levels of mannosan or galactosan [18, 19], whereas significantly higher levels are produced from the combustion of contemporary biomass. Furthermore different types of contemporary biomass, such as softwoods and hardwoods [20-22] and grasses and scrubland [23] have been shown to exhibit source specific mannosan to galactosan ratios.

Exposure to ambient PM pollution is now ranked 9th worldwide and 11th in Western Europe in the list of risks to public health [24] and concentrations of particulate pollution have been particularly problematic over the region in recent years, where there have been several episodes of extended

97 breaches of EU air quality limits. This study aimed to quantify current concentrations of
98 levoglucosan present in atmospheric PM in order to estimate levels of contribution of biomass
99 burning to total PM_{10} and to determine possible biomass sources. The study was carried out
100 between April 2013 and May 2015 as part of the Joint Air Quality Initiative Project [25] over which
101 time PM_{10} filters were collected at five locations in the North-West Europe region: Leicester (UK),
102 Wijk aan Zee and Amsterdam (the Netherlands), Antwerp (Belgium) and Lille (France), (Figure 1) and
103 levoglucosan levels quantified using a previously validated GC-MS method [26]. The sites selected
104 avoided the mores studied megacites such Paris or London with very high population densities in
105 order to attempt to capture a more typical representation of biomass derived PM_{10} levels that the
106 majority of the population are exposed to across the region.
107
108

Experimental

Aerosol Collection, PM_{10}

Samples were collected daily (24 h exposure) onto 47 mm quartz filters (Pall Tissuquartz™, 2500 QAT-UP) using a sequential sampler Sven Leckel SEQ47/50 for Antwerp, Lille and Leicester or a Derenda PNS 16 for Amsterdam and Wijk-aan-zee with a PM_{10} inlet, running at 2.3 m^3/h for 24h per filter. Filters were weighed before and after sampling in order to determine total PM_{10} collection. For pre- and post-sampling weighing filters were conditioned at 20 ± 1 ^{o}C and 50 ± 5 % relative humidity for 48 h, weighed, left for a further 24 h and then re-weighed.

Aerosol samples were collected at fixed air quality monitoring sites in Amsterdam, Antwerp, Wijk aan Zee, Lille and Leicester (Table 1). All Leicester measurements were taken at the Defra AURN urban background air monitoring site based at the University of Leicester (http://uk-air.defra.gov.uk/networks/site-info?site_id=LECU&view=View).

PM_{10} sampling at the fixed sites was carried out during a 14 month period (426 days) from 1 April 2013 to 31 May 2014, except for the site in Lille where the measurements started 2 months later (5 June 2013 to 31 May 2014; 361 days), and Leicester where measurements were continued until 31 May 2015 (791 days). Monosaccharide anhydrides (MAs) were quantified every day for the site in Leicester and every 6th day for the other fixed sites, with additional analyses on alternate days during network validation (see the dates in Table 2).

Network Validation with Mobile Monitoring Station

PM_{10} levels were validated with use of a mobile monitoring station also containing a Sven Leckel SEQ47/50 sampler which was sited adjacent to the sites at Leicester, Amsterdam and Antwerp as well as at an alternative site within a few kilometres of the fixed sites (Table 1). MAs were quantified on alternate days at the additional sites in Amsterdam (AD2), Antwerp (AP2) and Leicester (LE2) and also for the validation filters taken in the mobile station adjacent to the Leicester site (LE1).

Data Coverage

Table 2 shows the number of valid gravimetric PM_{10} results for the sampler at the permanent monitoring site and for the sampler in the mobile station when located adjacent to the fixed site or at another site in the city. Data average availability for gravimetric PM_{10} across the fixed monitoring sites was 91%, and varied from 77% in LL1S to 91-97% for the other sites. When the delayed start to filter collection was taken in to account in Lille, data availability increased to 91%.

Chemicals

Chemical standards of levoglucosan (1,6-anhydro-β-D-glucopyranose), N-methyl-N-(trimethylsilyl)trifluoroacetamide) (MSTFA) with 1% trimethylchlorosilane (TMCS), anhydrous pyridine, cyclohexane, 1-phenyldodecane, methyl β-D-xylopyranoside and methanol were purchased from Sigma (Poole, UK). Standards of mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan

(1,6-anhydro-β-D-galactopyranose) were purchased from Carbosynth (Compton, UK). Syringe filters were 0.45 µm PTFE filters from Agilent Technologies (Wokingham, UK).

Quantification of Monosaccharide Anhydrides by GC-MS

Levoglucosan, mannosan and galactosan were quantified using a validated GC-MS method described in detail by Cordell *et al* (2014) [26]. Filters were analysed in three monthly batches and stored in at -20 ^{o}C in accordance with the previously validated storage conditions. Briefly, MAs were extracted from 1 cm^2 punches (spiked with 100 ng of methyl β-D-xylopyranoside as internal standard) from filters by sonication in 1 ml methanol, extracts were filtered, dried then derivatized with MSTFA/1% TMCS for 1 h at 80^{o}C. 0.5 µl of the derivitization product was analysed using an Agilent 7890A GC and 5975C MS with CTC-PAL autosampler (Agilent Technologies, Wokingham, UK). Quality control samples were included every tenth sample (100/10 ng/sample of levoglucosan/mannosan and galactosan for summer samples, 500/50 ng/sample of levoglucosan/mannosan and galactosan for winter samples) along with a blank extracted filter sample. Calibration was carried out at the beginning of each batch of analysis and was conducted over the range 5-5000 ng/sample for levoglucosan and 1-500 ng/sample for galactosan and mannosan.

The mass spectrometer was operated in single-ion monitoring mode with the following ions monitored: *m/z* 92, 204, 217 and 333. Mannosan, levoglucosan and methyl β-D-xylopyranoside were quantified using the 204 ion with *m/z* 217 and 333 used for identity confirmation, galactosan was quantified using the 217 ion with *m/z* 204 and 333 used for identity confirmation.

Black Carbon Measurements

Atmospheric black carbon measurements were taken at the Leicester site using a Multiangle Absorption Photometer (MAAP) Model 5012 (Thermo Scientific) sampling at 1 m^3/h with a PM_{10} inlet and $PM_{2.5}$ sharp cut cyclone, measuring absorbance at 670 nm.

Results and Discussions

Leicester

Levoglucosan as a Biomass Burning Marker

Levoglucosan is the most abundant organic tracer produced from the combustion of biomass [17], and has been used for quantification of wood burning in a variety of studies across the world [6-10, 20, 22, 28-30]. It is suitable for use as a single marker species as non-biomass burning sources of levoglucosan are likely to be insignificant. Although initially thought to have very good atmospheric stability [14, 31], more recently there has been some concern over its potential degradation in high OH conditions [32, 33]. However, whilst this may have important consequences in tropical regions it is likely to have little effect in the North-West European area.

Biomass Burning in Leicester

Daily (24 h) PM_{10} filters were collected over the two year study period in Leicester, from which levoglucosan concentrations were quantified. Figure 2 shows the levels of levoglucosan measured across this time period. Two distinct periods of raised levels of levoglucosan can be discerned where biomass burning was raised, covering the period from November to March each year. For both years November saw the highest monthly averages of levoglucosan (126 ng/m^3 in 2013 and 140 ng/m^3 in 2014) followed by December (95 and 80 ng/m^3, respectively). Mean summer levels were 20 ng/m^3, and the mean concentration over the two year period was 45 ng/m^3. Leicester summer levels were similar to those determined in other studies across Europe which have also shown consistently low summer levels of levoglucosan in the order of 5-50 ng/m^3 [6-8, 28-30, 34].

Winter levels in Leicester (76 ng/m^3 for 2013, 72 ng/m^3 for 2014 December to February) are similar to those measured by Crilley *et al* [35] at various sites across London and the South East in January and February of 70-92 ng/m^3 in 2012, and but slightly higher than the averaged concentrations of 31-59 ng/m^3 detected by from Harrison *et al* [34] at multiple sites in London (2010-2011) and the Birmingham area. These measurements were, however, averaged over a longer season from November to March which could explain the lower levels. Leicester levels are, however, somewhat lower than those measured in another UK study in London 2009-2011 which reported January to February concentrations in the range of 162-190 ng/m^3 [10]. Levoglucosan concentrations in Leicester during the winter are also relatively modest compared to the concentrations reported for the same period at several other European cities, for example: winter levels in Austria were in the range of 190-860 ng/m^3 [20], in Belgium 130-640 ng/m^3 [7, 28, 29], in Czech Republic 326-572 ng/m^3 [30] and those in Aviero, Portugal were measured at 1290 ng/m^3 [6].

Figure 3 shows that the conditions under which high levoglucosan levels prevailed were at low wind speeds (<1 m/s) from all directions, or moderate winds (1-5 m/s) from the south-east. This suggests that levoglucosan and thus biomass burning PM is generally being emitted locally and that the housing to the south east is the dominant source of levoglucosan when winds exceed 1m/s.

The relationship between average daytime temperature and atmospheric levoglucosan concentration was examined, and can be seen in Figure 4. Whilst a general seasonal pattern can be

observed and all exceedances of 100 ng/m^3 (90th percentile) occurred at relatively low temperatures (<13^{o}C), other than on a seasonal level there appears to be little direct correlation between levoglucosan and temperature. This is indicative of the use of biomass burning in Leicester not as a primary heat source but for other purposes such as decorative or as a secondary heating source.

Other Monosaccharide Anhydrides

The application of levoglucosan as a sole marker for biomass combustion has been shown to be less accurate where there is the potential for emissions from burning of lignite to cause interference, and that the isomeric ratios with other MAs may be more specific [19]. To this end in this study mannosan and galactosan were simultaneously measured alongside levoglucosan. Mannosan is the second most abundant MA produced in biomass smoke and levoglucosan to mannosan (L/M) ratios can be used to help discriminate combustion sources. In previous studies the combustion of softwoods has typically yielded L/M ratios of 2.6-6.7 [22, 36, 37], whereas hardwood and lignite produce ratios that are significantly higher (13-24 for hardwoods [22, 36-39] and 31-90 lignite [19]). Incorporation of galactosan (G) concentrations can facilitate further discrimination as galactosan has been previously demonstrated to constitute a diagnostic marker for recent biomass burning [16]; L/(M+G) ratios of 1.8-2.8 [22, 36] provide further evidence of softwood sources.

The average L/M ratio of 2.8 and L/(M+G) ratio of 2.2 determined for Leicester in this study (Figure 5) are therefore in the range previously determined for combustion of mostly soft woods. Figure 5 also shows that there is excellent correlation between levoglucosan and mannosan and with mannosan and galactosan and that the relatively consistent ratio demonstrates a constant combustion source throughout the year. Some caution, however, should always be used when interpreting sources of MAs in complex environmental samples as the absolute monosaccharide release can be connected in part with the combustion regimes [40], with some uncertainty in the possible effects that this can have on isomer ratios [41].

Data Validation Using Duplicate Analysis

In order to assess the reliability and reproducibility of the data produced within the study, a mobile monitoring station was deployed to cross-validate the levoglucosan levels recorded at the Leicester fixed site. The mobile station was situated around 10 m from the fixed site and PM_{10} filters were collected at both sites using identical sampling equipment over 28 days from the 6th March 2014 to 4th April 2014. These data (see supplementary data) demonstrated excellent agreement between the two measurements, confirming the reliability of both the filter sampling and MA analysis methods.

Black Carbon and Wood Burning

Black carbon was also measured at the Leicester site over the period of the study using a MAAP 5012 measuring absorbance at 670 nm. Previous investigation has shown that black carbon formed from wood burning contributes to the absorbance at this wavelength, but traffic also makes a considerable contribution [42]. Figure 6 shows that when examined on a monthly averaged basis there is good correlation between levoglucosan and black carbon concentrations. However, when this is examined on a daily average basis it can be seen that whilst levoglucosan levels peak at weekends, BC levels are highest on working days. This demonstrates that at the Leicester site the BC

measurements are predominantly influenced by traffic BC emissions rather than those from biomass burning.

Quantifying PM from Wood Burning

When examining the effects of wood burning on air quality it is important to not only consider the absolute levels but also the contribution to PM as a whole. There is, however, considerable uncertainty associated with the correct factor to use in order to convert from a levoglucosan concentration to a PM_{10} mass. The absolute magnitude of this factor is affected by several variables including combustion source and combustion conditions. Schmidl *et al.* [22] investigated this in some detail and derived the conversion factor of 10.7, produced assuming a beech/spruce/briquette ratio of 2:7:1, and this factor has been used previously in several European biomass burning studies [7, 20]. For this study the 10.7 factor of Schmidl *et al.* was used owing to the prediction that woods burnt in the UK are likely to be predominantly softwoods and not dissimilar to those burnt in other nearby European locations. Other studies have used slightly different factors but most are of a similar value: *e.g.* Szidat *et al.* [43] use 10, Puxbaum *et al*. [6] 8.75, and Fuller *et al*. [10] used 11.

Using this conversion factor the daily contribution of wood burning to PM_{10} can be calculated (Figure 7), which again shows a distinct period of increased contribution between November and March both years. The average contribution to PM_{10} in Leicester over the two year of the study was 3.1 % (average PM_{10} concentration 0.49 μg/m^3), which rose in the winter period to 5.1% (0.77 μg/m^3). Several days, however, greatly exceeded the seasonal averages with 25 days exceeding 10 % contribution, the highest contribution being recorded on Christmas day 2013 where the percentage contribution peaked at 32%. However, the mass concentration was only 1.92 μg/m^3 with the high contribution caused by the low (6.1 μg/m^3) total PM_{10} concentration recorded on this day.

Comparison of Levoglucosan Levels Across NW Europe

In order to get a broader picture of how biomass burning levels varied across North-West Europe data collected from a further four sites in Belgium, the Netherlands and France were included in the second part of the study. To get an understanding of the composition of PM_{10} at all these sites, whilst keeping the sample numbers manageable, PM_{10} concentrations were measured every day but only every sixth filter was subjected to monosaccharide anhydride analysis. In order to compare the data sets every sixth day reading was used from the Leicester site in this analysis.

Figure 8 shows the average monthly concentrations of levoglucosan at the five sites across NW Europe for the study period April 2013 to May 2014. It can be seen that levels were similar across the sites throughout summer, but notable differences in winter occurred, with Lille having consistently the highest concentrations from November to May.

The presence of detectable levels of levoglucosan at all site during in summer is indicative of the presence of other contributing sources throughout the year other than domestic heating. These could include alternative domestic sources, such as garden waste burning, or wood fuelled patio heaters, as well as agricultural sources.

As previously discussed, levoglucosan concentrations in Leicester in 2013-2015 are lower than the majority of measurements taken across Europe, however, none of the sites considered were located in the largest cities often examined in such studies, such as London or Paris [5, 10, 34, 35, 44]. The sites considered offered an insight into wood burning in the urban environment removed from the largest cites with the most pronounced air quality problems; as despite this type of location housing large proportions of the population they have been generally less well studied. The highest levels, in Lille over winter are in the range of those measured in neighbouring Belgium (130-640 ng/m^3 [7, 28, 29]), and Antwerp shows somewhat lower levels than the ~300 ng/m^3 previously measured in the region during 2010/2011 [7]. Both the Dutch cities (Wijk aan Zee and Amsterdam) showed similar concentration and when averaged over the winter periods were, similar to Leicester with some of the lowest concentrations measured.

Contribution to Total PM_{10}

The average seasonal contribution of wood burning to total PM_{10} at all sites can be seen in Figure 9, calculated using a conversion factor of 10.7 [22]. A similar trend is seen as observed for the concentrations of levoglucosan, with Lille demonstrating the highest contribution to PM_{10} over the autumn, winter and spring periods 2013-2014 (no spring 2013 data were collected for Lille). Winter average contribution in Lille reached 11.6 % in winter 2013 with a mean PM_{10} mass concentration of 2.11 µg/m^3, whereas the other sites were notably lower, in the range 2.7-5.8 % (0.56-1.36 µg/m^3). Other studies have shown comparable levels at urban sites across Europe: *e.g.* Caseiro *et al*. [20] estimated that wood burning was responsible for around 10% of wintertime PM_{10} in Vienna, approximately 7-9 % (1.8 µg/m^3) of the wintertime PM mass concentration in London (2009 and 2010) originated from biomass burning [10] and in Flanders, Belgium wood burning has been estimated to contribute between 5 and 6 % of the annual mean PM_{10} in six cities [7]. There appears to be higher use of wood as a fuel source in certain rural areas and the contribution of biomass burning to PM_{10} can be particularly high in some areas in winter, *e.g.* in the municipality of Hamme, Belgium the contribution of biomass burning to the total mass of PM_{10} was recorded at 21.9 % [7], with an average of 7.5 µg/m^3 of PM produced by biomass combustion.

Although measured levels in 2013/2014 at the sites assessed average contributions are relatively low, on several days in the year they exceeded 20 % which, while not likely to cause regulatory breaches alone, may well offer a significant enough input to push total PM_{10} concentrations over the EU day limit value of 50 µg/m^3. The vast majority of particles emitted in wood smoke are below 2.5 µm [13], so the newly introduced $PM_{2.5}$ yearly limit of 25 µg/m^3 will likely be even more severely impacted. If biomass burning does increase as predicted by the EU forecasts [11] then it may start to become a significant obstacle in maintaining particulate pollution levels below legislative limits.

MA ratios

In order to assess how biomass sources varied across the sites throughout the year, monthly averaged L/M and L/(M+G) ratios were examined (Table 3). Across the sites the L/M ratios were in the range 2.1-6.7 and L/(M+G) 1.8-4.3, which is consistent with a predominantly softwood combustion source, as previously discussed for the ratios calculated for the Leicester site. Leicester showed the most consistent ratios throughout the year (as previously demonstrated in Figure 5)

indicating a largely consistent combustion source. More variation was seen at the other sites, with Lille having the largest range (2.8-6.7 L/M, 2-4.3 L/(M+G)) and the highest recorded ratios 6.7/4.3. All sites demonstrated an increase in both L/M and L/(M+G) ratios from the lowest values in July/August which increased into winter before subsiding again in spring. Although the ratios still imply a predominantly soft wood combustion source [19] it would appear that the source is changing subtly throughout the year. The baseline levels measured during the summer and autumn months are likely derived from sources other than domestic heating, such as garden bonfires, or agricultural waste disposal. The sources in winter, predominantly domestic heating, appear to have a higher hardwood contribution pushing the ratios up.

Network Validation-PM_{10}/Levoglucosan

Further network validation was carried out by comparison of mobile station PM_{10} measurements with fixed site measurements at Amsterdam, Antwerp and Leicester over a period of approximately one month (see Table 2 for periods measured). The results demonstrated (see Supplementary Information) that the correlation for the three sites visited by the mobile station was very good, although PM_{10} measurements were consistently slightly higher at the mobile station.

To examine spatial variation of PM_{10} and levoglucosan in the local environment, the mobile monitoring station was sited at an alternative location 1.2-6.2 km from the fixed site. Figure 10 shows that there is, for the majority of the time, a good agreement of PM_{10} and levoglucosan concentrations (analysed every 2nd day) between the sites. This is suggests that one urban background monitoring site is likely to be representative of biomass burning and PM_{10} concentrations throughout the considered urban environments.

At the Leicester site PM_{10} levels were significantly different on one day, and on another levoglucosan levels were also very different. The PM_{10} concentration recorded on 24/4/14 was significantly higher at the fixed site (100 $\mu g/m^3$ compared to 15 $\mu g/m^3$). On this day the weighing results for the filters fell within specified parameters and operational data for the PM_{10} samplers were normal. There was also no difference in levoglucosan concentration on this day, but K^+ was three time higher at the fixed site. The most likely conclusion from these data is that a very local source may have increased PM_{10}; most probably dust created by construction work that was being carried out in the proximity of the fixed site sampler on the date in question. On 18/4/14 there was a significantly raised level of levoglucosan at the mobile site compared to that recorded at the fixed site (48 compared to 12 ng/m^3); again this is most likely a very local source of burning which increased levoglucosan.

Long distance influence of Wood Burning

The potential influence of biomass burning emissions over long distances was investigated by correlation of levoglucosan concentrations between the different sites across Europe. A strong correlation (r^2 = 0.865, data not shown) was seen between the two closest cities Amsterdam and Wijk aan Zee (~25km apart), some degree of correlation is seen between Antwerp and Lille (r^2 = 0.65) and Antwerp and Amsterdam (r^2 = 0.53) which are around 100 km apart. Overall correlation decreased with distance (Figure 11), suggesting that the normal domestic use of biomass as a combustion source in one city is only likely to have an effect in the local region.

Extreme Burning Events

Easter bonfires are a tradition across large areas of Europe including Denmark, parts of Sweden, Finland, Germany, Switzerland, Austria and parts of the Netherlands and mass bonfire events such as these can have a widespread effect across extensive areas. Figure 12 shows how levoglucosan levels far exceeded seasonal averages on Easter day despite a lack of localised burning in the vicinity of the sites themselves, with only Leicester being far enough away to be unaffected. Although too far away to be affected by the Easter fires, the highest level of levoglucosan in Leicester over the entire study period was recorded on the 6th November 2014 (which corresponds to midnight onwards on Guy Fawkes Night - a traditional bonfire and fireworks festival in the UK) at 766 ng/m^3. This concentration is nearly double the next highest concentration observed. Unfortunately, no data was collected for Guy Fawkes Night the previous year, but there are likely to be significantly raised levels every year owing to the prevalence of bonfires on the preceding evening. These data show that biomass burning; despite having mostly significant effects locally has the potential to have wide ranging effects across Europe.

Sixth Day Sampling Validity Assessment

Data analysis for comparisons across the five sites was carried out using measurements taken from every sixth day filter, whereas at the Leicester site daily measurements were available. This enabled an assessment to be made regarding the representativeness of six day data as a substitute for daily sampling. Figure 13 shows the mean values obtained from the Leicester data, where averages are taken from daily filters compared to every sixth filter on the days used for the cross site study.

The approximation of the six day data was very good over the summer and spring periods, but showed higher error over autumn and winter; with December 2013 showing the largest error. This is most likely caused by the large variations in levoglucosan levels that occurred in December with levoglucosan ranging hugely from 10 to 438 ng/m^3. Despite the underestimation evident in the data the sixth day data still gives a good overall estimator of biomass burning levels for only a fraction of the analysis effort, and an accurate relative comparison between the different sites as the measurements were taken on the same days across all the sites.

Conclusions

This study represents one of the most extensive studies to date to examine the current effect biomass burning is having on air quality across Europe. The data collected demonstrates the existence of a distinct biomass burning period stretching from November to March across all sites in North West Europe, with Lille consistently showing the highest levels of burning throughout spring, autumn and winter. The highest contribution to PM_{10} also occurred in Lille in winter where it averaged 11.6%. The average winter PM_{10} contribution across all sites was 5.6%, which fell to below 1% in summer. Although these contributions seem relatively low currently, there are several driving forces including rising fuel costs and government renewable fuel schemes which are likely to cause increases in biomass burning derived PM_{10} pollution in years to come. A poor correlation between temperature and levoglucosan concentration was observed at the Leicester site, the site of most intense study, suggesting that wood is probably not being burnt as a primary domestic heat source at this location.

Data indicates that the detrimental effects of burning on air quality are only likely to be evident in the local region as poor correlation was observed between most locations; however, large organised burning events can cause much wider scale effects on air quality. Levoglucosan offers more reliable estimates of biomass burning than markers such as K^+ and black carbon which are subject to higher levels of interference from other sources. Furthermore the simultaneous measurements of other MAs allowed the determination of the primary combustion source. In this study isomer ratios suggested that softwoods were the mains source across the sites.

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Tables

Table 1 - Details of location of fixed sites and temporary monitoring/validation sites.

City	Site Code	Site name	Distance to main street (m)	Traffic intensity[a] (vehicles/day)
Amsterdam	AD1	Vondelpark	64	17000
	AD2	Nieuwendammerdijk	20	<300
Antwerp	AP1	Borgerhout	30	29500
	AP2	Stadspark	45	7800
Leicester	LE1	Leicester University	140	22500
	LE2	Brookfield	150	20500
Lille	LL1	Lille-Fives	35	NA
Wijk aan Zee	WZ1	Wijk aan Zee	70	NA

1 - fixed site and 2 - temporary site for mobile monitoring station.

[a] Mean traffic intensity at the nearest main street.

Table 2 - Number of exposed filters used for gravimetrical analysis of the PM_{10} mass concentration in the cross site comparison period. For the sampler at the fixed site, the data availability is given in brackets (fraction of 426 days of monitoring).

City	Fixed Site	Adjacent to site[b]	Alternative site[c]	Total
Wijk aan Zee (WZ)	397 (0.93)	-	-	397
Amsterdam (AD)	415 (0.97)	34	14	463
Antwerp (AP)	414 (0.97)	27	27	468
Leicester (LE)	388 (0.91)	28	35	451
Lille (LL)	328 (0.77[a])	-	-	328
Total	1942 (0.91)	89	76	2107

[a] Data availability of 0.91 during the actual monitoring period in Lille (05/06/2013 to 31/05/2014).

[b] AD: 10/04/2013 to 13/05/2013; AP: 10/09/2013 to 06/10/2013; LE: 06/03/2014 to 04/04/2013.

[c] AD: 15/05/2013 to 28/05/2013; AP: 08/10/2013 to 03/11/2013; LE: 06/04/2014 to 15/05/2013.

Table 3 – Monthly levoglucosan to mannosan (L/M) and levoglucosan to mannosan + galactosan (L/(M+G) ratios across all sites.

	Wijk aan Zee		Amsterdam		Antwerp		Leicester		Lille	
Month	L/M	L/(M+G)	L/M	L/(M+G)	L/M	L/(M+G)	L/M	L/(M+G)	L/M	L/(M+G)
Apr-13	3.3	2.6	3.7	2.7	3.8	2.8	3	2.4	NA	NA
May-13	3	2.4	3.4	2.7	3.6	2.7	2.7	2.2	NA	NA
Jun-13	2.9	2.4	2.8	2.2	3.5	2.7	3	2.4	2.8	2.3
Jul-13	2.1	1.8	2.4	1.9	3.5	2.5	3	2.3	3.3	2.2
Aug-13	2.4	1.9	2.8	2.2	3.6	2.7	2.6	2.1	2.9	2
Sep-13	2.6	2	2.9	2.3	3.1	2.5	3	2.4	3.2	2.5
Oct-13	3.2	2.3	4.1	3.2	3.9	2.9	3	2.4	3.1	2.3
Nov-13	4.1	2.8	4.2	2.9	4.4	3.2	3.4	2.5	5	3.5
Dec-13	5.2	3.5	4.7	3.2	6.1	4.1	4.2	2.8	6.7	4.3
Jan-14	4.5	3.1	4.6	3.1	6.1	4.1	3.7	2.6	5.7	3.8
Feb-14	4.1	2.9	5.5	3.6	5.6	3.8	3.2	2.2	5.4	3.7
Mar-14	3.7	2.5	4	2.7	4.6	3.1	4.6	3	4.7	3
Apr-14	4	2.6	4	2.6	3.9	2.7	3.7	2.5	4.4	2.8
May-14	6.1	3.2	4.8	2.8	4.4	2.7	3.1	2.2	5	3.2

Figures

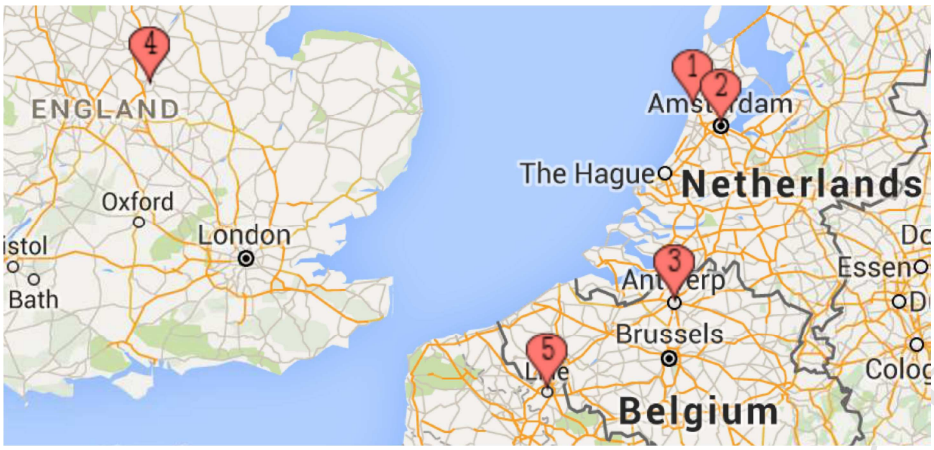

Figure 1 – Location of monitoring sites: 1 = Wijk aan Zee, 2 = Amsterdam, 3 = Antwerp, 4 = Leicester and 5 = Lille. Map data ©2015 Google.

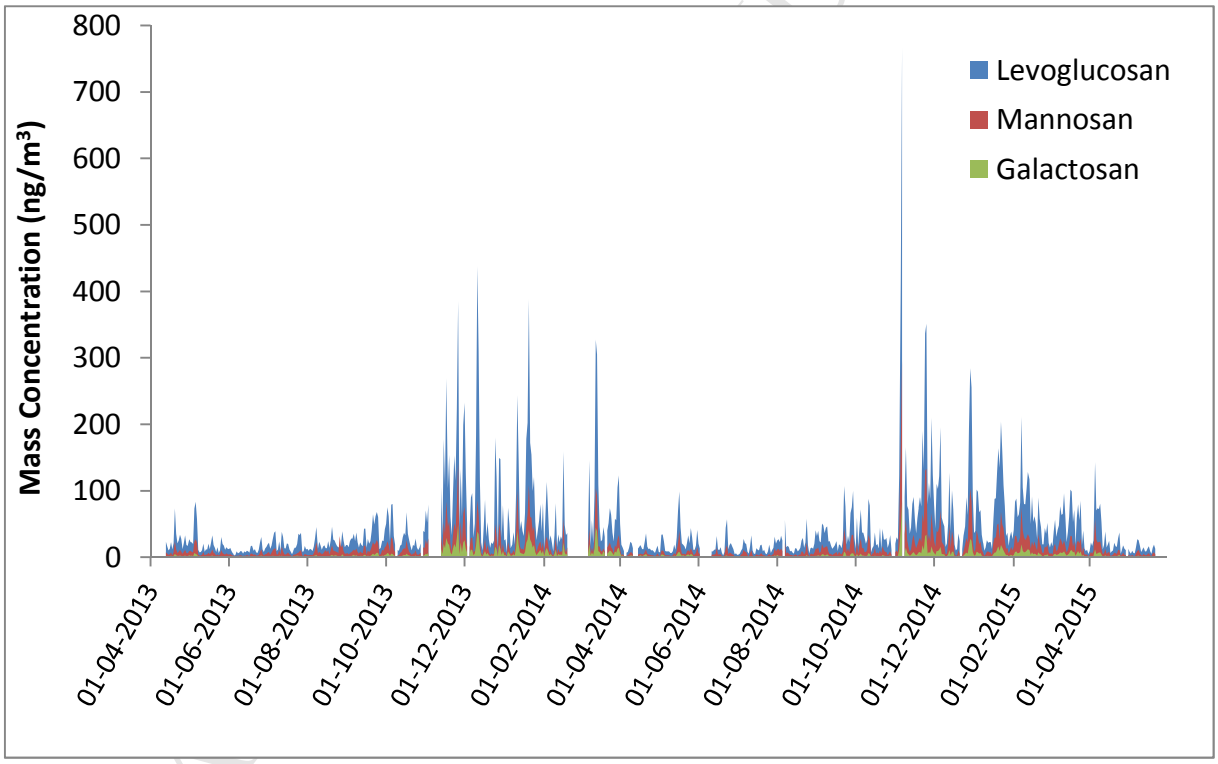

Figure 2 – Daily concentrations of monosaccharide anhydrides measured at the Leicester fixed site between April 2013 and May 2015.

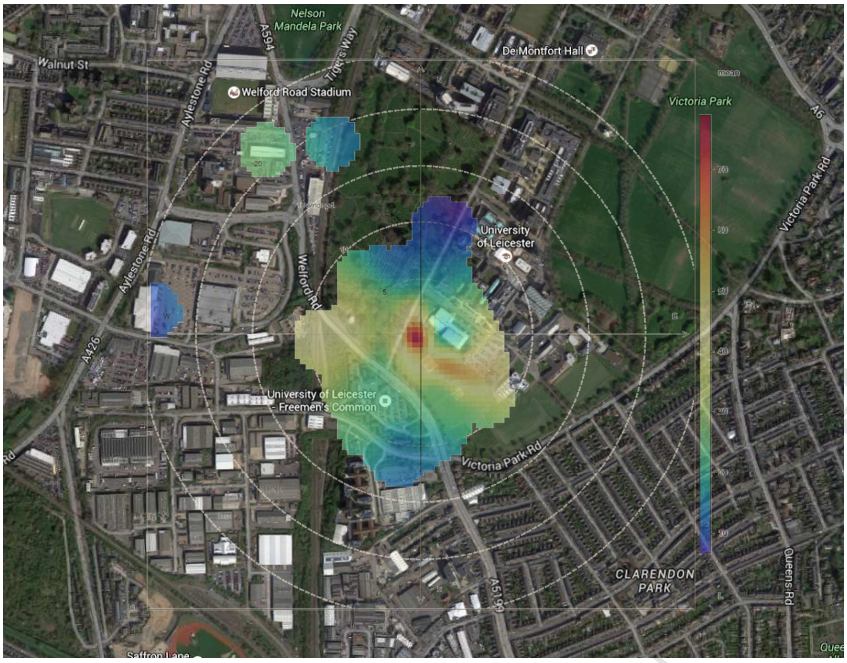

Figure 3 – Relationship between concentrations of levoglucosan concentration and wind measured at the Leicester urban background site between April 2013 and May 2015. Map data ©2015 Google.

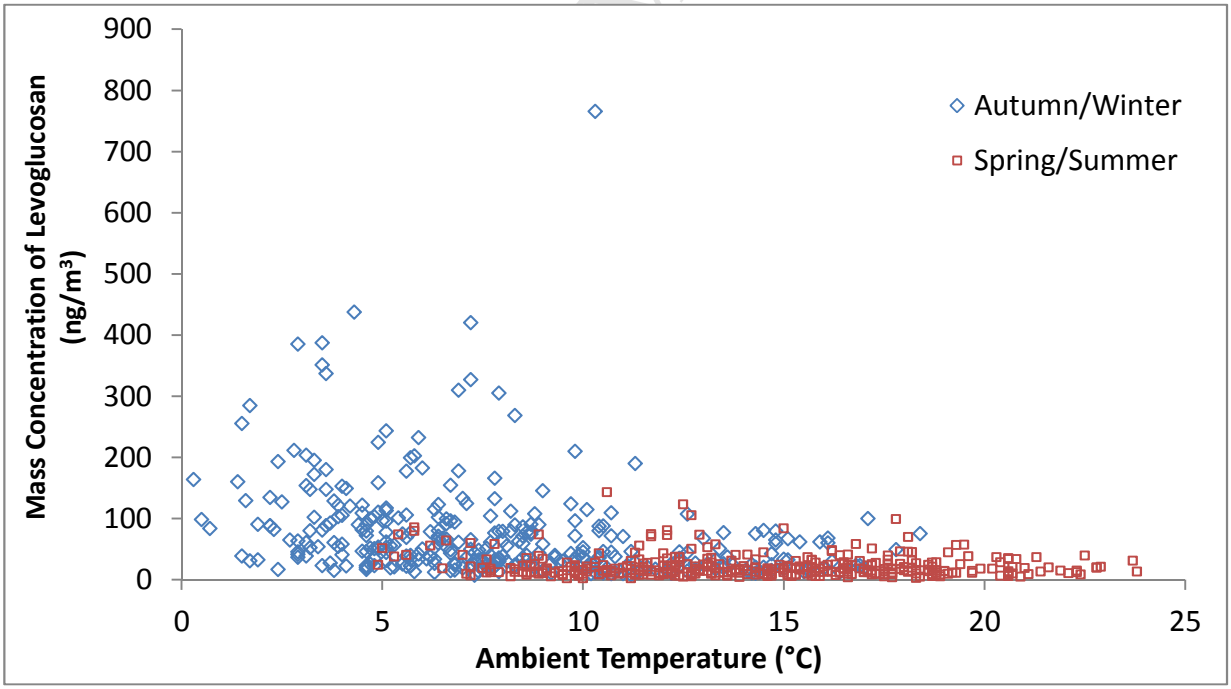

Figure 4 – Relationship between levoglucosan concentration and average daily temperature, measured at the Leicester site.

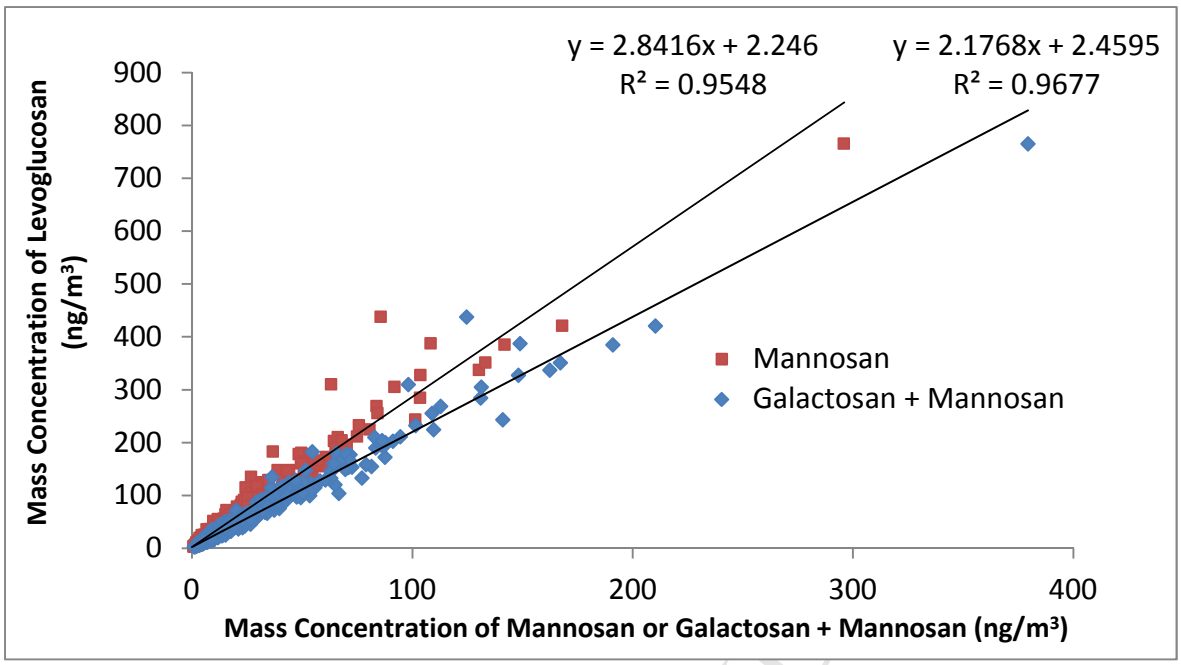

Figure 5 – Correlation of levoglucosan with minor monosaccharide components mannosan and galactosan, measured at the Leicester site.

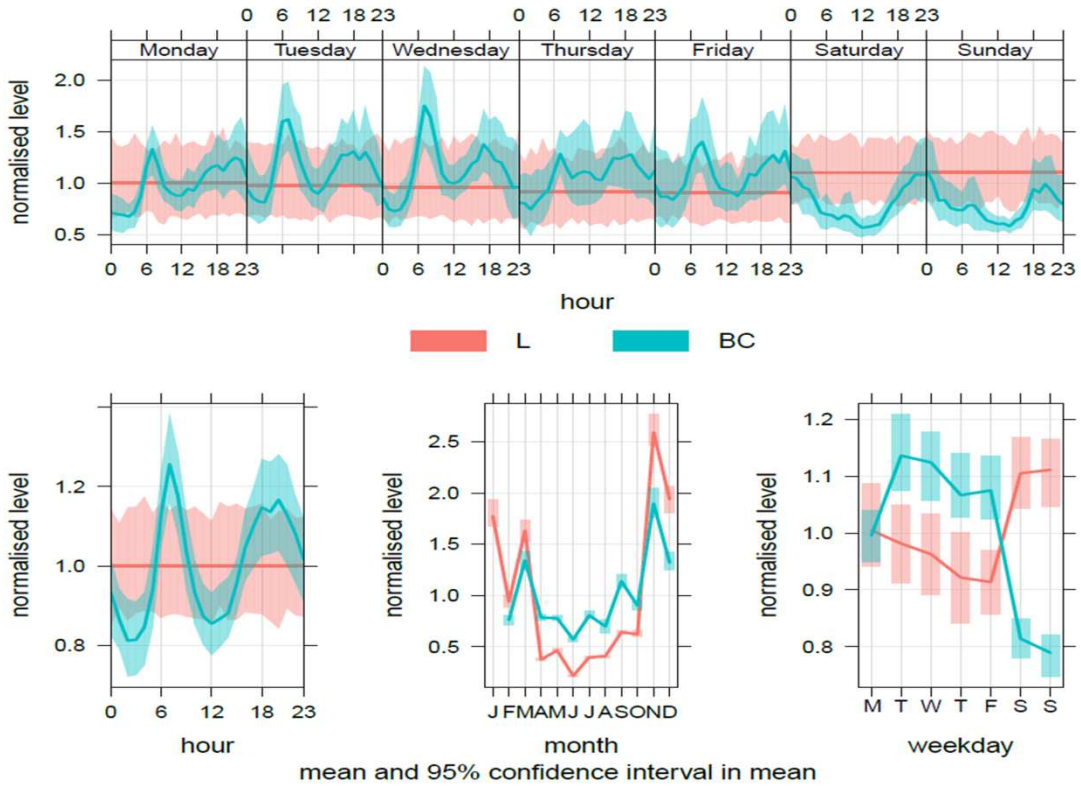

Figure 6 – Temporal daily, weekly and monthly variation of atmospheric black carbon (BC) at 670 nm and levoglucosan (L) concentrations measured at the Leicester site.

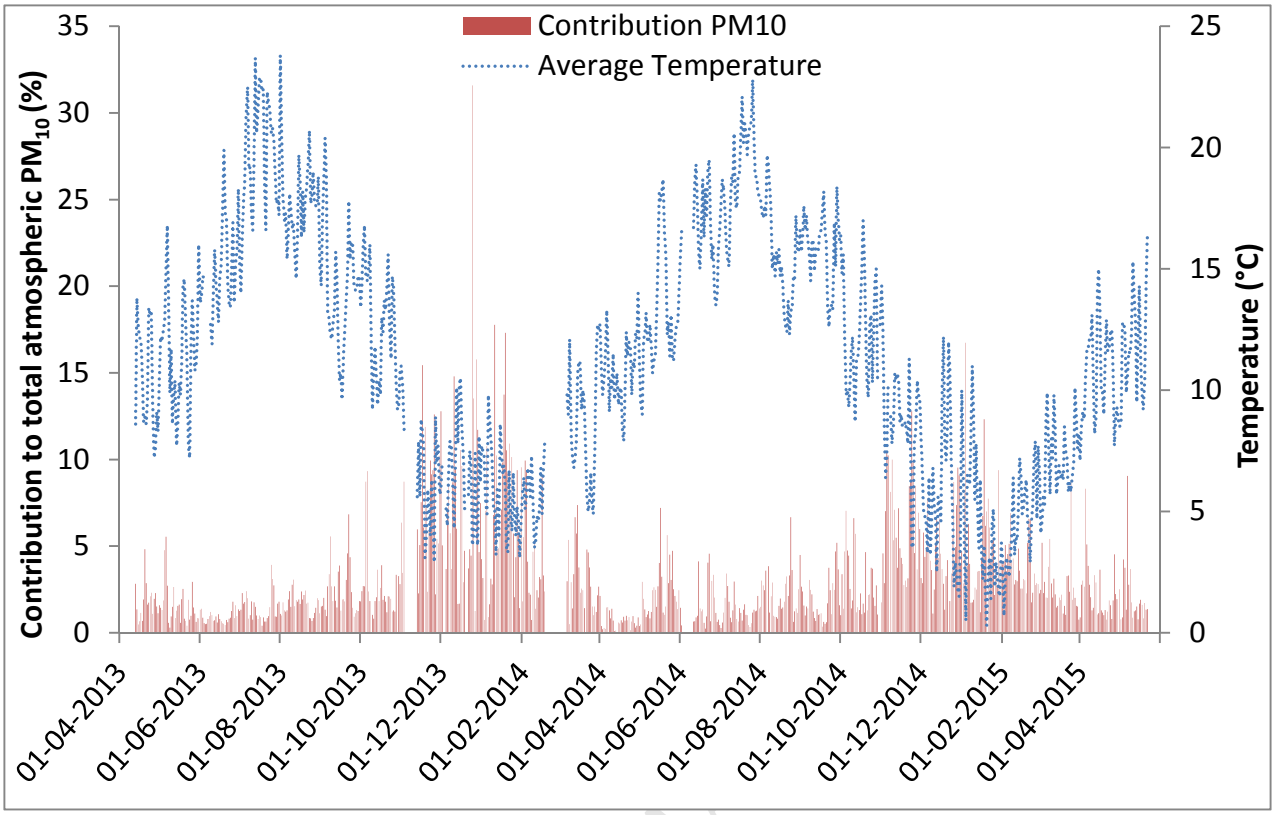

Figure 7 – Contribution of wood burning to total PM_{10} in Leicester calculated using a conversion factor of 10.7 as determined by Schmidl et al [22].

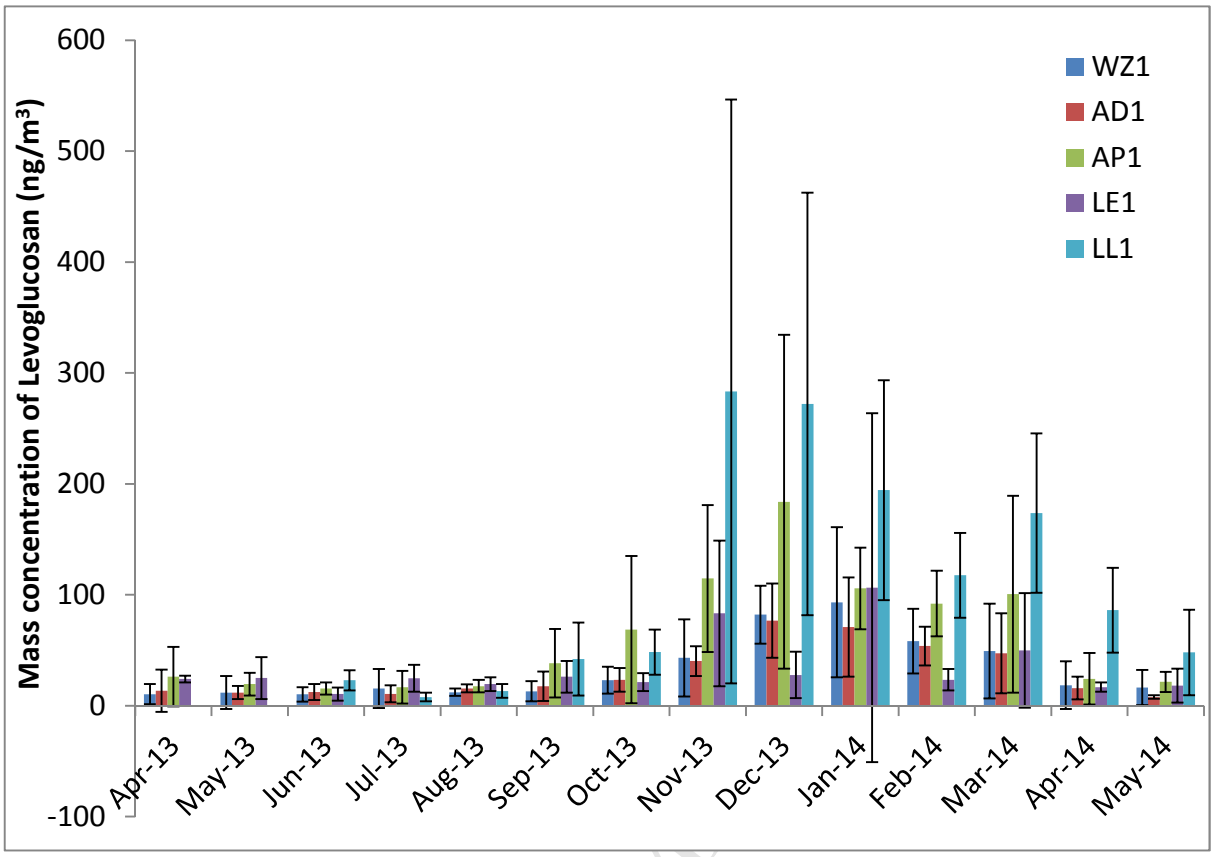

Figure 8 – Mean (± standard deviation) levoglucosan concentrations across all five NW European sites measured from every sixth day PM_{10} filters. WZ1 = Wijk aan Zee, AD1 = Amsterdam, AP1 = Antwerp, LE1 = Leicester, LL1 = Lille. N.B. Easter data excluded from averages.

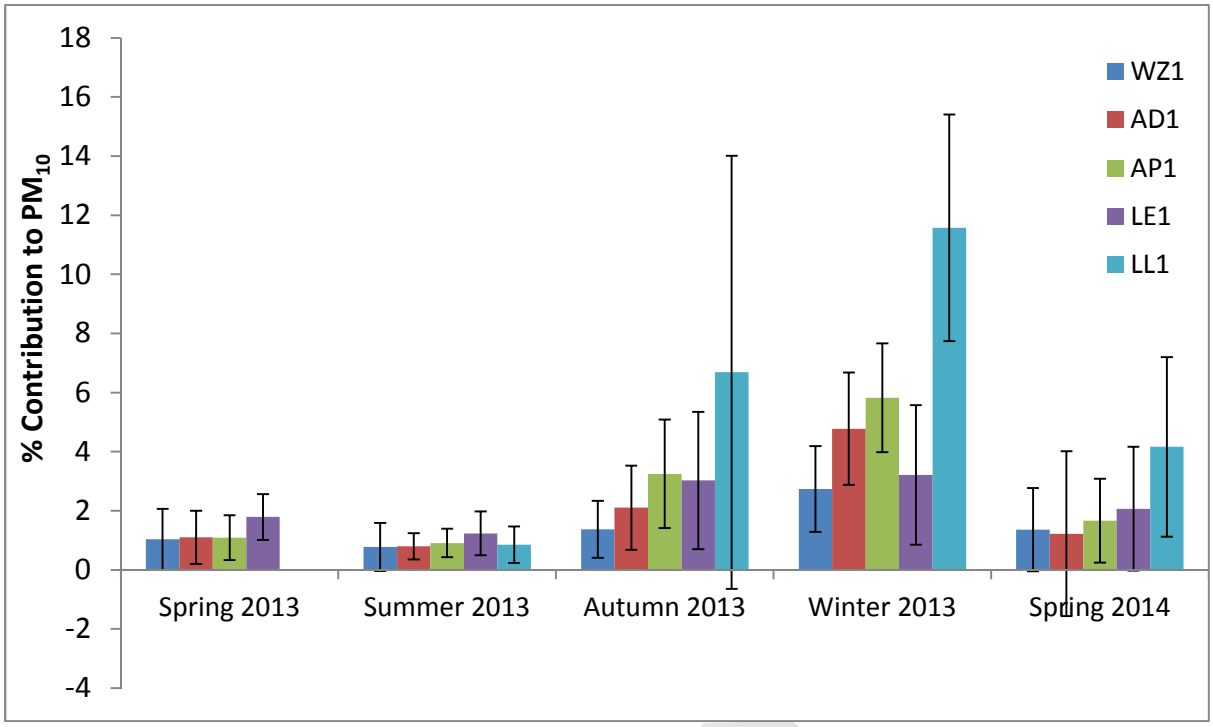

Figure 9 – Mean (± standard deviation) seasonal contribution of wood burning to PM_{10} across NW European sites measured from every sixth day PM_{10} filters. WZ1 = Wijk aan Zee, AD1 = Amsterdam, AP1 = Antwerp, LE1 = Leicester, LL1 = Lille.

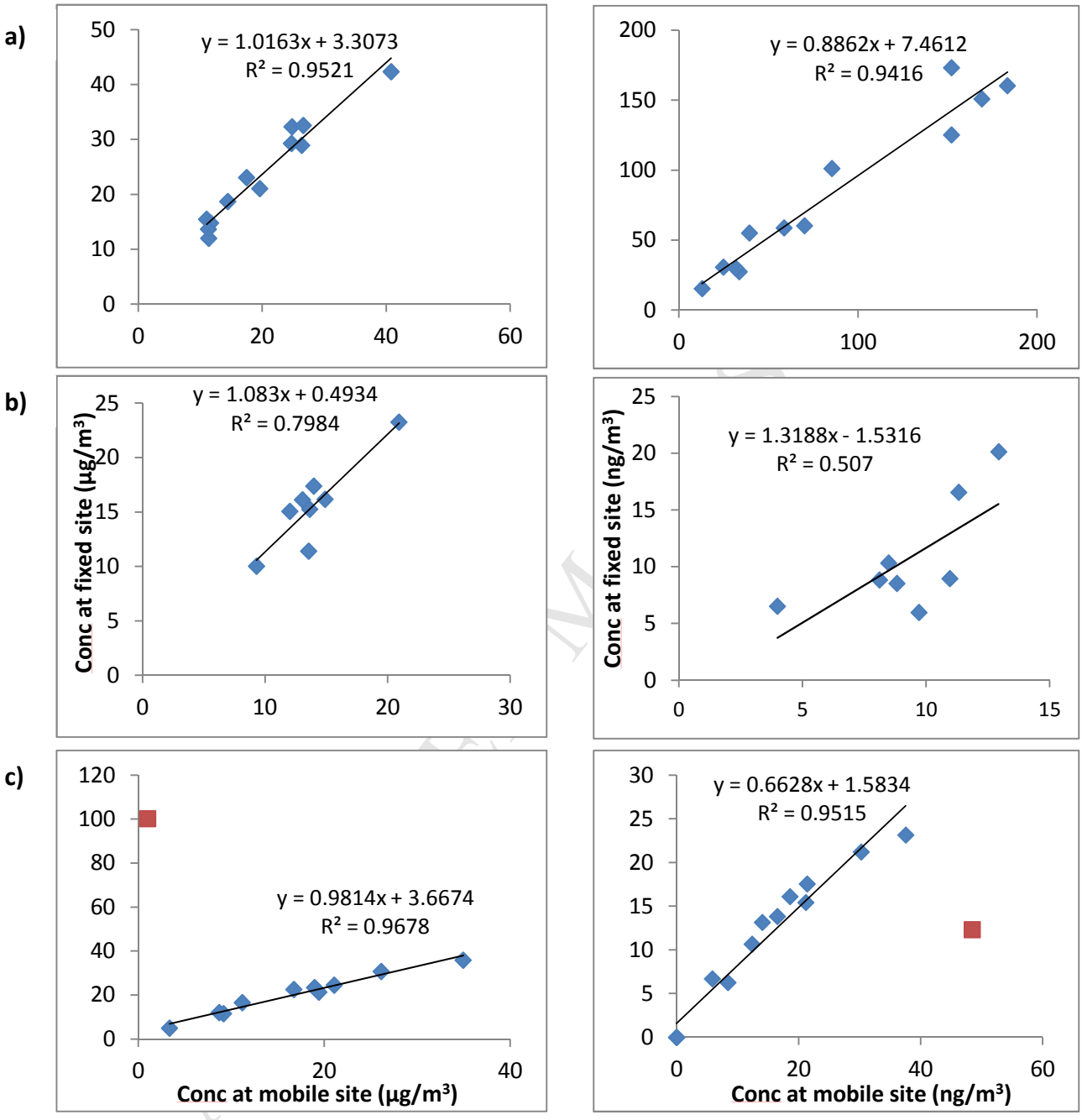

Figure 10 – Correlation of PM_{10} (left-hand column) and levoglucosan measurements (right hand column) between those taken at the a) Amsterdam b) Antwerp c) Leicester fixed site and the mobile station measurements taken 1.2-6.2 km away (see Table 1). 24/4/14 removed from PM_{10} correlation, and 18/4/14 from levoglucosan correlation for Leicester data (points shown in red).

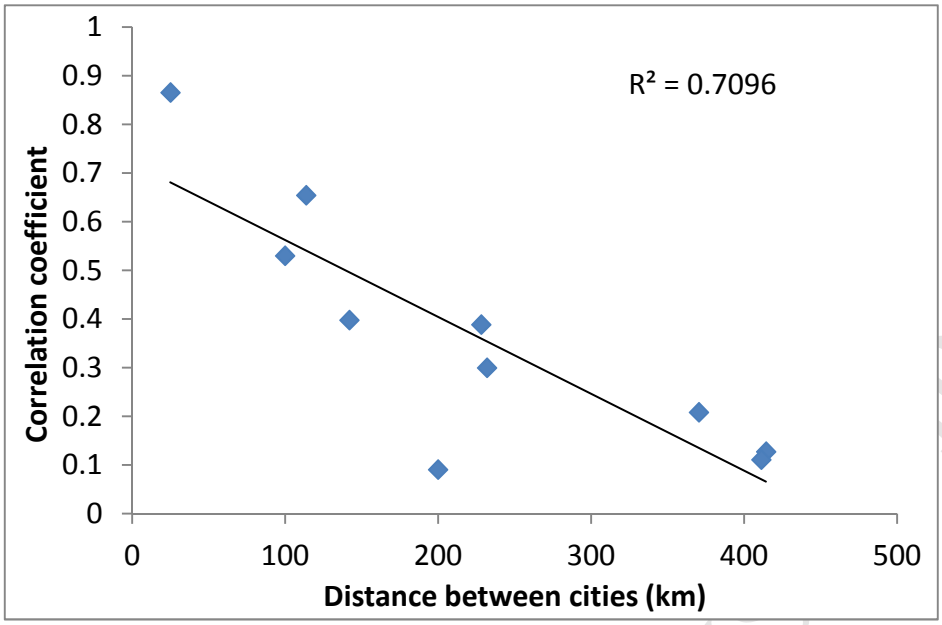

Figure 11 – Correlation between the correlation coefficient of levoglucosan concentration between cities and the distance between them.

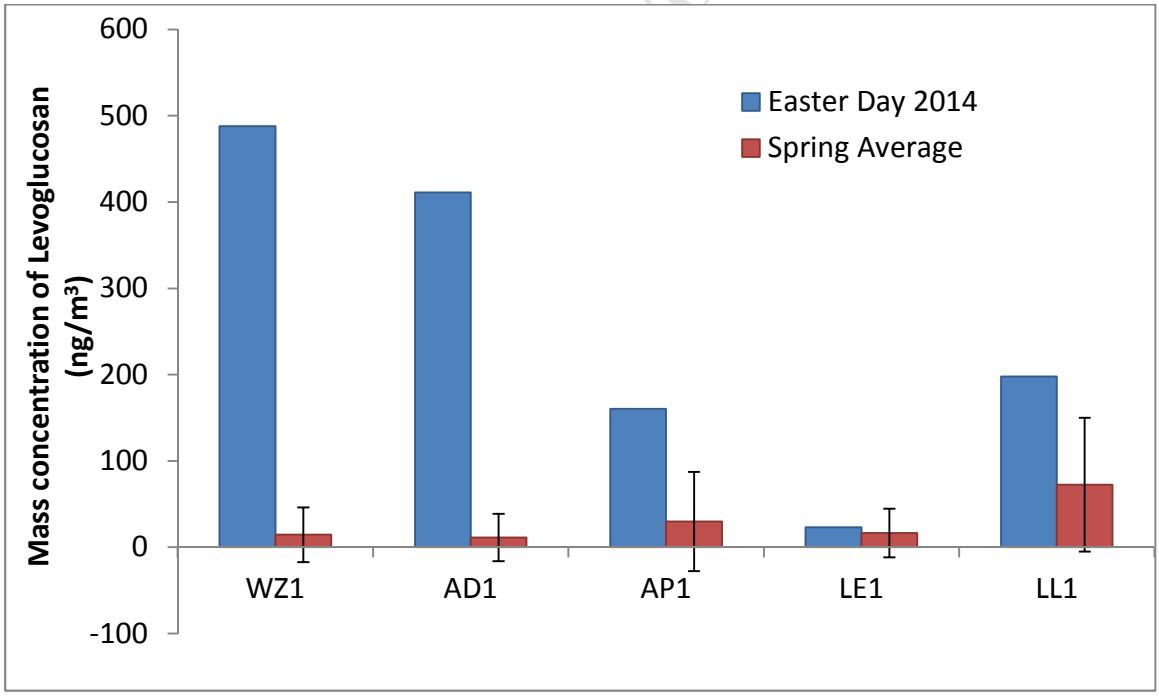

Figure 12 – Levoglucosan levels recorded on Easter day across the five fixed sites as compared to the seasonal average. WZ1 = Wijk aan Zee, AD1 = Amsterdam, AP1 = Antwerp, LE1 = Leicester, LL1 = Lille.

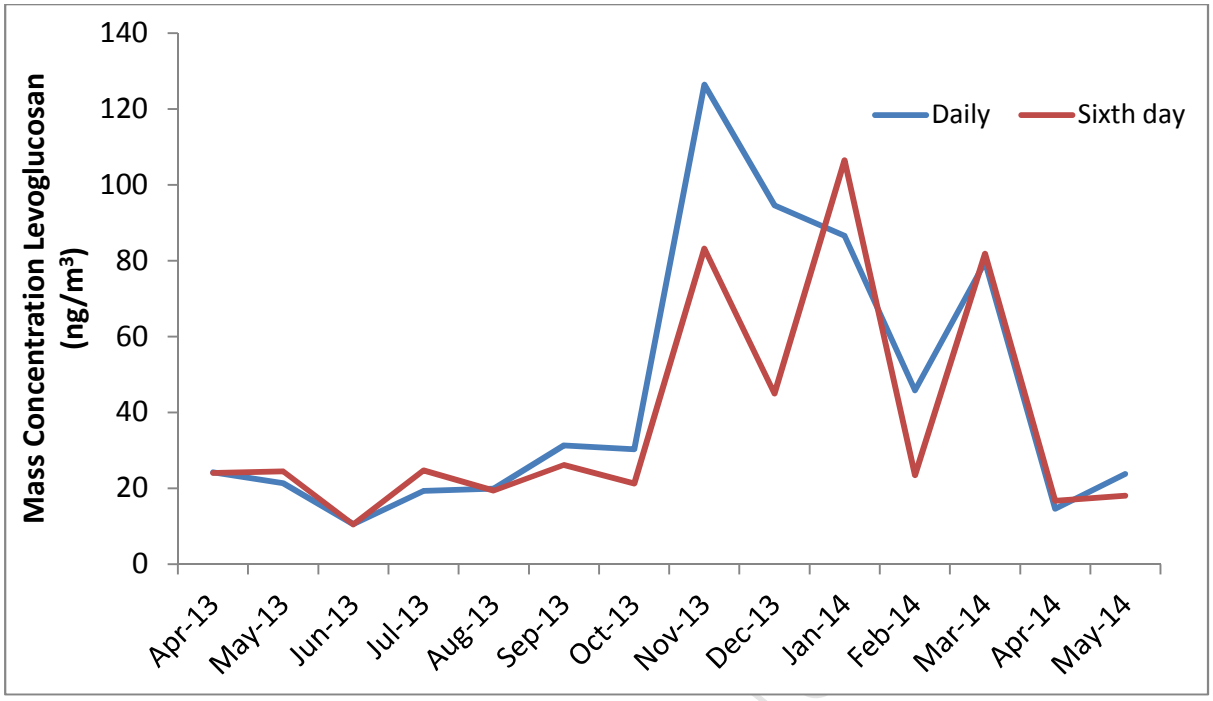

Figure 13 – Comparison of average levoglucosan levels calculated from daily data and every sixth day data at the Leicester site.

Highlights

- Biomass burning has the largest contribution to PM_{10} between November and March.
- The contribution of biomass burning in winter to PM_{10} ranges from 2.7% to 11.6%.
- Poor temperature correlation shows biomass burning is not a primary heating source.
- Effects of burning on air quality are normally only likely to be evident locally.
- Large organised biomass burning events can threaten air quality on a wider scale.