Atmos. Chem. Phys. Discuss., 14, 13491–13527, 2014
www.atmos-chem-phys-discuss.net/14/13491/2014/
doi:10.5194/acpd-14-13491-2014


Atmospheric Chemistry and Physics Discussions



# Spatial variations and development of land use regression models of levoglucosan in four European study areas

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Received: 20 February 2014 – Accepted: 30 April 2014 – Published: 23 May 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

**Abstract**

Relatively little is known about long term effects of wood smoke on population health. A wood burning marker – levoglucosan – was measured using a highly standardized sampling and measurement method in four study areas across Europe (Oslo, the Netherlands, Munich/Augsburg, Catalonia) to assess within and between study area spatial variation. Levoglucosan was analyzed in addition to other components: $PM_{2.5}$, $PM_{2.5}$ absorbance, $PM_{10}$, polycyclic aromatic hydrocarbons (PAH), nitrogen oxides ($NO_x$), elemental and organic carbon (EC/OC), hopanes, steranes and elemental composition. Measurements were conducted at street, urban and regional background sites. Three two-week samples were taken per site and the annual average concentrations of pollutants were calculated using continuous measurements at one background site as a reference. Land use regression (LUR) models were developed to explain the spatial variation of levoglucosan using standardized procedures.

Much larger within than between study area contrast in levoglucosan concentration was found. Spatial variation patterns differed substantially from other measured pollutants including $PM_{2.5}$, $NO_x$ and EC. Levoglucosan had the highest spatial correlation with ΣPAH ($r = 0.65$) and the lowest with traffic markers – $NO_x$, Σhopanes/steranes ($r = -0.22$). The correlation of levoglucosan with potassium (K), which is also used as a wood burning marker, was moderate to low (median $r = 0.33$). Levoglucosan concentrations in the cold (heating) period were between 3 and 20 times higher compared to the warm period. The contribution of wood-smoke calculated based on levoglucosan measurements and previous European emission data to OC and $PM_{2.5}$ mass were 13 to 28 % and 3 to 9 % respectively in the full year. Larger contributions were calculated for the cold period.

The median model $R^2$ of the LUR models was 60 %. In Catalonia the model $R^2$ was the highest (71 %). The LUR models included population and natural land related variables but no traffic associated variables.



In conclusion, substantial spatial variability was found in levoglucosan concentrations particularly within study areas. Wood smoke contributed substantially to especially wintertime $PM_{2.5}$ OC and mass. The low to moderate correlation with $PM_{2.5}$ mass and traffic markers offers the potential to assess health effects of wood smoke separate from traffic-related air pollution[1].

## 1 Introduction

Human exposure to air pollution has been associated with a range of health effects (Brunekreef and Holgate, 2002; Pope and Dockery, 2006). Particle matter (PM) with diameters smaller than 10 or 2.5 µm ($PM_{10}$, $PM_{2.5}$, respectively) is the most used parameter for assessment of air quality in epidemiological studies. However, PM is a chemically complex mixture and it has been suggested that observed adverse health effects depend on PM chemical composition (Stanek et al., 2011; Kelly and Fussell, 2012). Epidemiological studies have started to assess chemical composition of particles, but few studies have assessed the relationship between specific organic components and adverse health effects.

Biomass combustion is an important source of ambient particle matter and carbonaceous aerosol (Naeher et al., 2007). There are studies reporting acute and short term

[1]Abbreviations: ESCAPE, European Study of Cohort for Air Pollution Effects; TRANSPHORM, Transport related Air Pollution and Health impacts – Integrated Methodologies for Assessing Particulate Matter; EC/OC, elemental/organic carbon; PAH, polycyclic aromatic hydrocarbons; B[a]P, benzo[a]pyrene, GIS, Geographic Information Systems; LUR, Land Use Regression; $NO_x$, nitrogen oxides; $NO_2$, nitrogen dioxide; $PM_{2.5}$, mass concentration of particles less than 2.5 µm in size; $PM_{2.5}$ absorbance, measurement of the blackness of $PM_{2.5}$ filters, this is a proxy for elemental carbon, which is the dominant light absorbing substance; $PM_{10}$, mass concentration of particles less than 10 µm in size; RB, regional background; S, Street; EPA, United States Environmental Protection Agency; LUR, Land Use Regression; RMSE, Root Mean Squared Error.

effect on human health (Barregard et al., 2008; Bølling et al., 2009). Other studies presented evidence of toxicity of wood smoke based on in vivo (Thorning et al., 1982; Dubick et al., 2002) and in vitro (Leonard et al., 2000; Asita et al., 1991) experiments. Little is known about long-term health effects of wood smoke exposure (WHO, 2013). Karr et al. found an increased risk of infant bronchiolitis associated with wood smoke combustion (Karr et al., 2009). The most important sources of wood smoke are indoor cooking, forest fires, agricultural burning and residential heating.

Levoglucosan is a well-accepted tracer for wood burning in ambient air (Simoneit, 2002). This anhydrosugar is formed during pyrolysis of materials containing cellulose and hemicellulose. It is concentrated mostly in fine fraction of particulate matter (Simpson et al., 2004). Its specificity, photochemical stability and significant emissions in wood smoke allows for its reliable concentration assessment (Schkolnik and Rudich, 2006; Simoneit et al., 1999). Because of its stability and concentration in the fine fraction, levoglucosan concentrations may be affected by regional sources. Concentrations of levoglucosan have been measured in a variety of areas across Europe, but studies differ widely in the season of measurements, the type of location e.g. remote, rural or urban, PM size fraction and sampling method (Puxbaum et al., 2007; Caseiro et al., 2009; Caseiro and Oliveira, 2012; Reche et al., 2012; Maenhaut et al., 2012; Fuller et al., 2014). Annual average concentrations of levoglucosan reported across Europe varied significantly from a few till hundreds of ng $m^{-3}$ (Puxbaum et al., 2007). Clear seasonal variation has been reported with higher concentrations found in the cold season (Reche et al., 2012; Maenhaut et al., 2012). The variation may be due to differences in wood burning, but methodological differences may contribute as well.

Land use regression models (LUR) are used to model spatial variation of the annual average concentration of a pollutant mostly as a tool for exposure assessment of cohorts included in epidemiological studies (Hoek et al., 2008). The most modeled pollutants are $PM_{2.5}$, $PM_{10}$ and the traffic markers $NO_2$, PM absorbance and EC (Beelen et al., 2013; Eeftens et al., 2012a). There are few LUR models for pollutants with another origin than traffic. Recently, LUR models were developed for elemental



composition in 20 European study areas (de Hoogh et al., 2013). Three North American studies presented a LUR for wood smoke (Larson et al., 2007; Su et al., 2008; Smargiassi et al., 2012). Larson et al. and Smargiassi et al. used mobile monitoring of $PM_{2.5}$ and $PM_1$ respectively as a proxy for wood smoke, while Su et al. used levoglucosan monitoring for LUR model development. To our knowledge LUR models have not yet been developed for levoglucosan in Europe. Development of LUR models would be useful for studying the intra-urban variation of wood smoke PM.

In four European study areas we measured ambient concentrations of levoglucosan. The study areas were part of two European projects: ESCAPE (European Study of Cohort for Air Pollution Effects) and TRANSPHORM (Transport related Air Pollution and Health impacts – Integrated Methodologies for Assessing Particulate Matter). Both projects provide advanced knowledge on the impact of outdoor air pollution on human health in Europe. In the framework of the projects concentrations of the following pollutants were measured: $NO_x$, $NO_2$, $PM_{2.5}$, $PM_{10}$, $PM_{2.5}$ absorbance and elemental composition. Results of these measurements and LUR models for these pollutants have been published (Beelen et al., 2013; Eeftens et al., 2012a, b; de Hoogh et al., 2013; Cyrys et al., 2012). In a subset of 10 study areas the concentrations of elemental and organic carbon (EC/OC) and polycyclic aromatic hydrocarbons (PAH) were determined (Jedynska et al., 2014).

To assess wood-smoke health effects in epidemiological studies we need spatial variation between and/or within study areas of a sufficient magnitude. The spatial patterns of wood smoke should not be too highly correlated with other pollutants (e.g. EC), to allow separation of health effects. We finally need to be able to model the spatial variation to allow exposure assessment for a large number of residential addresses. The aim of the work reported here was to determine the spatial contrast of levoglucosan within and between four European study areas – Oslo, the Netherlands, Munich/Augsburg and Catalonia. The second aim was to assess the contribution of wood smoke to OC and mass by seasonal and full year. The third aim of our study was to assess the relationship of levoglucosan with $PM_{2.5}$ mass, other organic components, another

biomass marker – potassium (K) - and traffic markers analyzed within the ESCAPE and TRANSPHORM projects. Our fourth aim was the development and evaluation of LUR models of levoglucosan.

## 2 Methods

### 2.1 Sampling campaign

Levoglucosan measurements were added to the standardized ESCAPE sampling campaign, described in detail previously (Eeftens et al., 2012b; Cyrys et al., 2012). In Oslo and Munich/Augsburg levoglucosan measurements were performed at all 20 ESCAPE sampling sites with particle measurements, in the large study area of Catalonia at all 40 sites. In the Netherlands, levoglucosan measurements were performed at 16 of the 40 ESCAPE particle sites, because of lack of the additional impactors needed for levoglucosan sampling. All study areas included regional and urban background and major street sites (Table 1).

At each sampling site, three two-weekly samples were collected over a period of one year. Samples were taken during three different seasons: winter, summer and intermediate season – either spring or autumn. Due to lack of the sampling equipment in Munich/Augsburg, no samples were taken in the winter (December–February). For extended $PM_{2.5}$ characterization two samples were collected: one on a Teflon coated glass fiber filter (T60A20, Pallflex) for analysis of specific organic components (PAH, hopanes/steranes) (Jedynska et al., 2014) and one on a quartz filter (QMA,Whatman) for EC/OC, oxidative potential and levoglucosan quantification.

### 2.2 Sampling site selection

In each study area, three types of sampling site were defined: regional background (RB), urban background (UB) and street location (S). Street locations were defined as locations at a major road with more than 10 000 vehicles passing per day. Urban and



regional background locations were sites with less than 3000 vehicles passing per day within a radius of 50 m. Regional background locations were mostly located in small villages. The partners in all study areas used identical sampling protocols and criteria for the selection of sampling sites.

### 2.3 Analytical methods

#### 2.3.1 Levoglucosan

All measurements were performed centrally at TNO. 2.5 $cm^2$ of each quartz filter was used for measurements of levoglucosan. The analytical method for levoglucosan was described before by Simpson et al. (2004). Briefly, each filter was extracted in ethylacetate with 0.5 % triethylamine in an ultrasonic bath for 1 h. Further, extracts were derivated with silating reagent (TMSI).

Levoglucosan was measured with gas chromatography in combination with mass spectrometric detection in electron impact mode (Agilent 6890/5973N GC/MS). Levoglucosan quantification is based on component identification by retention time, specific ion ratios and an internal standard (SRM2267). The total expanded uncertainty amounts 30 %.

#### 2.3.2 EC/OC, PAH, hopanes, steranes, $PM_{2.5}$, $NO_2$ and elemental composition

Analytical and sampling methods and spatial variability across Europe of $PM_{2.5}$, other organic components and elemental composition measured in the four study areas where published in detail previously.

The analytical methods of EC/OC, PAH and hopanes/steranes were published by Jedynska et al. (2014). In summary, 1 $cm^2$ of each quartz filter was used for EC/OC analyses, which were completed via a thermal-optical analyzer (Sunset Laboratory, Inc., Oregon, USA). The EUSAAR2 protocol was used for the temperature settings. PAH and hopanes/steranes were sampled on T60A20 filters. Filters were

extracted via an accelerated solvent extraction method (ASE) with toluene. Furthermore, extracts were fractioned into three fractions via a silica column. This separated hopanes/steranes from PAH. 16 EPA PAH and 13 hopanes/steranes were analyzed via gas chromatography in combination with mass spectrometric detection (GS/MS) in electron impact mode (GC/MS EI, Agilent 6890/5973N).

$PM_{2.5}$ mass and absorbance were determined on Andersen 37 mm 2 mm pore size Teflon filters (Eeftens et al., 2012). All filters were pre- and post-weighed at a central laboratory (IRAS, Utrecht University, Utrecht, the Netherlands). Reflectance of all filters was measured in the central laboratory and transformed into absorbance according to (ISO (International Standardization Organization) 1993). $NO_2$ was measured with Ogawa passive samplers (Cyrys et al., 2012). The analysis is based on the Saltzman method and was performed in one central lab.

$PM_{2.5}$ Teflon filters were analyzed for elemental composition using energy dispersive X-ray fluorescence (XRF) (de Hoogh et al., 2013). Analyses were performed at Cooper Environmental Services, Portland, OR, USA.

### 2.4 Quality control

To maximize comparability of the measurements in different countries, sampling and measurement procedures were conducted according to standard protocols (Eeftens et al., 2012b; Cyrys et al., 2012). Each filter was placed in a separate filter holder and petri dish and was sent centrally to project partners from one laboratory. Five field blanks were taken in the Netherlands to calculate the methods' detection limits and correct individual results by subtracting the mean field blank. The limit of detection (LOD) was calculated as three times the standard deviation of five field blank measurements. All methods used at TNO have been validated according to the Dutch national norm (NEN-7777, 2003).



### 2.5 Data analysis

All measurements' results were analyzed centrally at TNO. Statistical analyses were performed with the SPSS statistical program (IBM SPSS Statistics 20). Spatial variation was presented as minimum, maximum, range percentage of the mean, where range is the difference between maximum and minimum. Because of a few outliers we also calculated the 25th and 75th percentiles. Outliers were defined as concentrations higher than: P75 + 1.5 · (P75 – P25), where P75 and P25 are 75th and 25th percentile, respectively. For LUR model development the more rigorous definition of outlier was used: P75 + 4 · (P75 – P25).

Student's *t* tests were used to calculate the difference (and significance) between site types and between seasons. To assess spatial relationships between components the Spearman rank correlation was calculated.

Individual measurements were used to assess seasonal differences in levoglucosan concentrations. Previous studies have used either strict summer/winter or warm to cold period comparisons. For comparison we used both definitions, one comparing samples taken in the summer (June–August) and in the winter (December–February). In Munich/Augsburg no samples were taken in the winter. We also analyzed differences based on all individual measurements divided into the warm (April–September) and cold period (October–March).

The contribution of wood smoke to the measured OC and $PM_{2.5}$ was calculated by using previously published conversion factors from levoglucosan to OC and mass in wood smoke (Puxbaum et al., 2007; Maenhaut et al., 2012; Caseiro et al., 2009). We used factors of 5.59 and 10.7 to calculate wood smoke OC and wood smoke mass respectively (Maenhout et al., 2012). These factors have been derived from emission testing in Austria and may be different elsewhere in Europe. The levoglucosan content of wood smoke depends on the type of wood burnt (soft or hard wood), temperature and type of burning process. The estimated uncertainty in levoglucosan content has been estimated to be about 30 % (Maenhout et al., 2012).

### 2.6 Adjustment for temporal variability

The three two-week samples were used to estimate the annual average level of levoglucosan. For practical reasons, it was not possible to collect samples simultaneously at all sites of each study areas. Due to temporal variation in air quality, the simple average from the concentrations in the three sampling periods at the sampling sites could reflect both spatial and temporal variation. In order to correct for temporal variation, a reference site was continuously measured in each study area during a full year including the sampling period. The reference site was located at a background location, away from local emissions. Our correction procedure followed the modified ESCAPE procedure used for EC/OC, PAH and hopanes/steranes (Eeftens et al., 2012b; Cyrys et al., 2012).

At the reference sites, the following components were measured: $NO_x$, $NO_2$, $PM_{2.5}$, $PM_{2.5}$ absorbance and $PM_{10}$. Levoglucosan and EC/OC, PAH and hopanes/steranes were not analyzed at the reference sites because of lack of sampling equipment. To adjust for temporal variation, we identified which component measured at the reference site correlated best temporally with levoglucosan. First, the temporal correlation was calculated for each site between levoglucosan and the standard pollutants based upon three samples. Second, the median correlation per study area was calculated and the standard component with the highest median correlation with levoglucosan was used for correction. As we had only three samples per site available, site-specific correlations were not robust whereas the median is more robust. We thus used one component for the entire study area. Because another pollutant was used for correction of levoglucosan, we used the ratio method as we did for EC/OC, PAH and hopanes/steranes instead of the difference method, which was the default in ESCAPE. Ratios were calculated between the concentration of the standard pollutant in each sampling period and the annual average at the reference site. These ratios were used as an adjustment for all sites in a specific sampling period. A high correlation was found between results corrected with the ratio and difference methods for $PM_{2.5}$, $PM_{2.5}$ absorbance, $PM_{10}$



and PMcoarse in three study areas (Stockholm County, the Netherlands/Belgium and Catalunya) (Eeftens et al., 2012b).

The correction was performed for each of the three sampling periods at a specific site and finally, the average of the adjusted concentrations of these three periods was used to calculate the annual average.

### 2.7 Predictor data for LUR model development

A description of predictor variables have been presented in detail (Beelen et al., 2013; Eeftens et al., 2012a). Briefly, the predictor variable describe potential emission sources such as traffic, industry or population density. The values of predictor variables were determined for each sampling site using a geographical information system (GIS). Geographic data were obtained from two sources: central and local. Central data sets included: information on roads (EuroStreets version 3.1), land use (CORINE land cover 2000), altitude (SRTM 90 m Digital Elevation Data), and population (enhanced EEA population density data using CORINE land cover 2000). When available, local GIS data were collected on road network, traffic intensity, land use, population density and altitude. Each variable was calculated for several circular buffers around the sampling site. Detailed description of calculated variables including buffers and a priori specified direction of effect on the pollutant concentration are presented in online Supplement Table S1.

### 2.8 LUR model development

LUR models were developed centrally at IRAS. We followed the ESCAPE method (Beelen et al., 2013; Eeftens et al., 2012a, de Hoogh et al., 2013). Briefly, adjusted annual average concentration of levoglucosan and predictor variables were used for LUR development. A supervised stepwise method was used to obtain the linear regression model with the highest explained variance ($R^2$). At every step the variable with the highest $R^2$ was added to the model if it improved model's adjusted $R^2$ by at least 1 %

and had the same effect direction as decided a priori e.g. higher population density predicts higher levoglucosan concentration or higher green/natural area variable predicts lower levoglucosan concentrations. Further, models were evaluated for statistical significance (variables removed when $p$ value > 0.10), collinearity (variables with Variance Inflation Factor (VIF) > 3 were removed) and influential observations (models with Cook's $D > 1$ were further examined). The final models were evaluated by leave-one-out cross validation (LOOCV) Morans' $I$ ($p > 0.05$) was calculated to indicate possible spatial autocorrelation in the residuals.

## 3 Results

The main focus of presented results is on adjusted annual average concentrations, except Sect. 3.2 which shows seasonal variation. In the online Supplement Table S2 the components selected for temporal adjustment of levoglucosan concentrations are presented. In Oslo, the absorbance of $PM_{2.5}$ measured at the reference correlated best with levoglucosan concentrations. In the Netherlands, Munich/Augsburg and Catalonia $NO_x$ measured at the reference correlated best with levoglucosan concentrations. Correlations ranged between 0.83 and 0.99 (Table S2 in the Supplement), documenting that the temporal variation of levoglucosan was well characterized by other components. Adjusted and unadjusted annual averages were very highly correlated ($r$ between 0.97 and 0.99, online Supplement Table S3). This documents that the adjustment did not change the results much.

The limit of detection (LOD) of the levoglucosan measurements was 1.3 ng m$^{-3}$. All samples were above the LOD. The spatial variation within and between study areas is presented in Fig. 1 and Table 2. Differences between site types are presented in Fig. 2 and in Supplement (Table S4).



### 3.1 Within and between study area contrast

Levoglucosan concentrations were highest in Munich/Augsburg – 102 ng m$^{-3}$ and lowest in Catalonia 64 ng m$^{-3}$ (Fig. 1, Table 2) but the differences in levoglucosan concentrations between study areas were not statistically significant. There was high within study area variation. In the Netherlands range to mean ratio was 132 % and in Catalonia the ratio was the highest – 562 % (Table 2). In Catalonia two outliers were identified: one at a street location in Barcelona with only two measurements, both taken in the colder part of the year with high levoglucosan concentrations. The second outlier was a regional background site in Girona with two out of three very high concentrations of levoglucosan measured in February and November. In Oslo an urban background site was identified as an outlier due to extremely high concentration found in the sample taken in November. In Munich/Augsburg a regional background site situated in the small town Erding was detected as an outlier due to very high levoglucosan concentration in the summer sample.

In Catalonia levoglucosan levels were higher in the Girona area than in Barcelona and Sabadell (Fig. S1). In the Netherlands the highest concentrations were found in the Groningen area and the lowest in the Rotterdam (Fig. S1). These spatial patterns were opposite to the patterns observed for traffic-related pollutants.

Differences between site types were mostly not significant (Table S4, Fig. 2), consistent with levoglucosan not being emitted by motorized traffic.

There are significant differences between levels of levoglucosan fraction in $PM_{2.5}$. The highest fraction of levoglucosan in $PM_{2.5}$ was found in Oslo (9.51 ng (µg $PM_{2.5}$)$^{-1}$) (Fig. 1b). The outliers for the fraction are the same sites as for levoglucosan concentrations per m$^3$. The site in Oslo with the highest levoglucosan concentration also had the highest levoglucosan fraction in $PM_{2.5}$ but was not a statistical outlier.

### 3.2 Seasonal differences

Due to lack of the sampling equipment in Munich/Augsburg, no samples were taken in the winter (December–February). In the other three study areas the average number of samples was: 15 in the summer and 17 in the winter. In all three study areas levoglucosan had significantly higher concentrations during winter (Fig. S2). In Oslo, Catalonia and the Netherlands the winter/summer ratio were 42.9, 41.9 and 17.3 respectively.

Comparison of all measurements in two periods (cold and warm), showed higher concentrations during the cold period but the ratio were smaller than for the winter/summer comparison (Fig. 3). Cold/warm concentration ratios in Oslo, Catalonia, the Netherlands and Munich/Augsburg were 19.8, 9.4, 3.2 and 3.0 respectively.

Also during the warm period several high levoglucosan levels were measured in all study areas.

### 3.3 Relationships between components

Spatial correlations between levoglucosan and other components differed substantially between the study areas (Table 3). In Oslo the highest correlation between levoglucosan and all components was found. In all areas, the highest correlation was found with ΣPAH and B[a]P with median correlation coefficients of 0.65 and 0.58, respectively. Levoglucoan – PAH correlations were highest in the Northern Europe city of Oslo and lowest in south European Catalonia. The lowest correlation was found between levoglucosan and traffic markers: Σhopanes/steranes and $NO_x$ (median $r = -0.22$). A relatively poor correlation was found between K in $PM_{2.5}$ and levoglucosan (median $r = 0.33$). The correlation between K in $PM_{10}$ and levoglucosan was even slightly lower (median $r = 0.27$).



### 3.4 Contribution of wood smoke to OC and $PM_{2.5}$ mass

The calculated contribution of wood smoke to measured OC was between 13 and 28 % in the full year and between 24 and 77 % in the cold period (Table 4), suggesting that wood smoke is an important contributor to OC in the fine fraction. The calculated contribution of wood smoke to measured $PM_{2.5}$ was between 4 and 11 % in the full year, increasing to between 9 and 28 % in the cold period, suggesting that wood smoke also moderately affects fine fraction mass.

### 3.5 Land use regression modelling

For all four study areas a LUR model could be developed. In Catalonia data from two sites, detected as outliers, were excluded from LUR model development. With these two sites included, LUR model development for Catalonia was not possible. In Table 5 LUR models are presented as well as models' $R^2$, LOOCV $R^2$ and root-mean-square error (RMSE). All models had moderate $R^2$. The lowest $R^2$ was found in Oslo ($R^2 = 0.59$) and the highest in Catalonia ($R^2 = 0.71$). LOOCV $R^2$ was higher than 50 % only in Catalonia. On average LOOCV $R^2$ was 11 % lower than adjusted $R^2$. In the Netherlands, Catalonia and Munich/Augsburg the variables representing green and natural areas were used. The negative direction of ß's of those variables (higher levoglucosan concentrations with less green/natural areas) was chosen a priori. In Oslo and Munich/Augsburg variables describing population were also used. No spatial autocorrelation of residuals was found (Morans'I $p > 0.05$).

## 4 Discussion

Substantial spatial contrasts were found within four study areas in levoglucosan concentrations but the differences between study areas were not statistically significant. Spatial variation patterns differed substantially from other measured pollutants including $PM_{2.5}$, $NO_2$ and EC, offering the potential to assess health effects of wood smoke

separate from traffic-related air pollution. Levoglucosan correlated only moderately with K, another often used marker for wood smoke. Levoglucosan concentrations in the cold (heating) period were between 3 and 20 times higher compared to the warm period. The contribution of wood-smoke calculated based on levoglucosan measurements and previous European emission data to OC and $PM_{2.5}$ mass were 13 to 28 % and 3 to 9 % respectively in the full year. Larger contributions were calculated for the cold period. For four study areas LUR models for levoglucosan could be developed with a moderate explained variance (median $R^2$ = 60 %).

A strength of our study was the standardization in every stage of the project. Samples were taken across Europe with the same equipment, analyzed in one laboratory, annual averages were calculated the same way and LUR models were developed centrally and according to a standardized protocol. This allowed us to obtain comparable results in four European study areas, assess differences between and within study areas and in the following step to apply those results in exposure assessment.

### 4.1 Contrast within and between study areas

There were no statistically significant differences in annual average levoglucosan concentrations between the four study areas, in contrast to concentration patterns of traffic-related pollutants ($NO_x$, $PM_{2.5abs}$, EC, ∑hopanes/steranes) and $PM_{2.5}$ mass which had the highest concentrations in Barcelona (and other southern European areas) and the lowest concentrations in Oslo (and other Northern European areas) (Cyrys et al., 2012; Eeftens et al., 2012c). PAH concentration also had similar levels in southern and northern Europe (Jedynska et al., 2014). In the cold period, levoglucosan concentrations were about two times higher in Oslo than in the other three study areas, consistent with the expected use of wood for heating. Although in general levoglucosan concentrations tend to be higher in Northern Europe a review table of published studies showed that this was not consistently found (Reche, 2012). Higher levoglucosan concentrations may occur outside Oslo and other major North-European cities where wood is more often used. High wintertime levoglucosan concentrations (900 ng $m^{-3}$) have indeed been



reported for the small town of Lycksele in Northern Sweden (Reche, 2012). A second explanation for the modest contrast across Europe is the contribution of forest fires and agricultural burning which is more common in Southern Europe (Reche, 2012).

The large variability in average levoglucosan concentrations in our study is consistent with previously reported substantial differences in levoglucosan for different sites in Europe (Reche, 2012). The comparison is limited as studies differ widely in season of measurements, often winter, one winter month or forest burning periods (Caseiro, Oliveira, 2012; Reche et al., 2012; Pio et al., 2008). Studies further differ in location, ranging from large urban areas to high altitude sites. Few studies have compared concentrations across countries. Puxbaum et al. reported annual levoglucosan average concentration for six rural background site across Europe (Puxbaum et al., 2007). The concentrations varied from 5.2 ng $m^{-3}$ in the Azores to 309 ng $m^{-3}$ in Hungary. A study at 7 urban and rural sites in Flanders reported annual median concentrations between 69 and 95 ng $m^{-3}$ for five sites (Maenhout et a. 2012), very comparable to our findings. Very high correlations of daily values at these sites were found, explained by the importance of regional wood burning and increased burning of wood on the same (cold, winter) days at all sites (Maenhout et al., 2012). At one coastal site the annual median was 34 ng $m^{-3}$ related to more impact of cleaner maritime air. At the site selected specifically to have wood burning in homes near the site, the median was 200 ng $m^{-3}$. Wood burning near our measurement sites likely explains some of the differences in levoglucosan annual concentration between individual sites e.g. in Catalonia minimum levoglucosan was 2.7 ng $m^{-3}$ and two highest levels exceeded 300 ng $m^{-3}$. We do not have information on wood burning near our sites. Our concentrations are in the low end of the range reported for annual average concentrations for three Austrian regions 120 (Vienna) to 480 (Graz) ng $m^{-3}$ (Caseiro et al., 2009). In the UK annual average levoglucosan concentrations were low – about 9 ng $m^{-3}$ (Harrison, Yin, 2010).

The variability between individual sites within study areas shows that it is not possible to represent population exposure to wood smoke in a city or region with one

pollutant concentration. As for traffic-related pollution, intra-urban exposure estimates are needed (Sect. 4.3).

### 4.2 Seasonal variations

Higher levoglucosan concentrations in winter or cold periods compared to summer or warm periods have been found consistently in previous studies (Caseiro, Oliveira, 2012; Giannoni et al., 2012). The reasons for higher concentrations of levoglucosan in winter include higher pollutant emissions (domestic wood burning heating systems) and poorer dispersion because of less vertical mixing during winter. As the winter/summer ratios for levoglucosan are substantially higher than observed for traffic-related pollutants for which source strength does not show much seasonal variation (Jedynska, 2014), increased source strength contributes to the levoglucosan increases. In our study, the highest seasonal difference was found in the coldest study area – Oslo, consistent with the fact that in Scandinavian countries it is very common to use wood for residential heating. A high cold / warm season ratio was also found in Catalonia in southern Europe. An explanation might be the absence of central heating resulting in burning wood for heating during the cold season, during relatively cold days. A study at one site in Barcelona also found very large differences between winter (60 ng $m^{-3}$) and summer (95 % of samples below the detection limit of 2 ng $m^{-3}$) (Reche, 2012). Levoglucosan concentrations were attributed to regional burning as in Barcelona city only very few homes have wood burning units (Reche, 2012). Puxbaum et al. found a similar cold / warm ratio in Aveiro, Portugal – 12.5 using the same way of dividing results onto two 6 month periods: warm and cold. In the two study areas located in the central Europe (considering North to south direction): the Netherlands and Munich/Augsburg the cold / warm ratio was the lowest – about 3. That is in line with the results from the same part of Europe (Puxbaum et al., 2007; Caseiro et al., 2009). In the Austrian study, winter/summer ratios of 6–8 were found. In Flanders, much higher winter/summer ratios (∼ 30) were reported (Maenhout et al., 2012). Differences in weather circumstances during sampling likely explain some of the variability across studies as



wood burning is often not the main source of heating and predominantly occurs on cold, winter evenings (Maenhout et al., 2012).

### 4.3 Contribution of wood smoke to OC and PM mass

Our calculated contribution of wood smoke to measured OC and $PM_{2.5}$ mass compares well with previous studies. A study in three Austrian regions reported wood smoke contributions to OC and $PM_{10}$ mass of 18–38 % to OC and 5–13 % to $PM_{10}$ mass for annual averages (Caseiro et al., 2009). The wood smoke contribution increased to 31–70 % and 7–20 % for winter OC and $PM_{10}$ mass averages. The highest contributions were found in the rural and smaller towns (Caseiro et al., 2009). The study in Flanders reported wood smoke contributions to OC and $PM_{10}$ mass of 20–36 % to OC and 5–13 % to $PM_{10}$ mass for annual averages (Maenhout et al., 2012). The wood smoke contribution increased to 36–60 % and 9–22 % for winter OC and $PM_{10}$ mass averages. The conversion factor used in our study assumes that mostly softwood (e.g. spruce) is burnt (Maenhout et al., 2012). If hardwood is used, higher conversion factors apply and we may have underestimated the wood smoke. Collectively, the results of our study and previous studies conducted in other areas of Europe document that wood smoke significantly contributes to fine particle concentrations in Europe. As wood burning occurs more on days with high particle concentrations from other sources due to unfavourable meteorological conditions, the contribution to the exceedance of the short-term $PM_{10}$ limit value was even higher than the contribution to the winter average (Maenhout et al., 2012).

### 4.4 Correlation with other components

We found a relatively low spatial correlation between levoglucosan and potassium (K) in $PM_{2.5.}$ Two studies in Barcelona and Austria reported high correlations between K and levoglucosan ($r$ = 0.7–0.8), but these studies reported the temporal correlation measured at one or a few sites (Reche, 2012; Caseiro et al., 2009). In our study, the

temporal correlation between K and levoglucosan was high as well ($r$ = 0.6–0.9, Table S5), reflecting especially similar seasonal behavior. The low spatial correlation may be due to more sources than wood burning contributing to K (Pio et al., 2008; Puxbaum et al., 2007; Caseiro et al., 2009; Reche et al., 2012). Other sources of K are soil, seawater, meat cooking and waste incinerators (Giannoni et al., 2012; Urban et al., 2012). Furthermore, we measured total K using XRF whereas only the fraction of water soluble K is considered as a tracer for wood smoke (Pio et al., 2008). Finally, the relatively low spatial variation of potassium within study areas, especially has contributed to low correlation with levoglucosan. Our study suggests that care is needed to interpret spatial variation of K as reflecting wood burning emissions.

The highest correlation was found between levoglucosan and ∑PAH and B[a]P (0.51–0.89). Wood burning is known to be one of the PAH sources (Ravindra et al., 2008). The correlation with ΣPAH was highest in Oslo and lowest in Catalonia, probably related a combination of higher wood smoke emissions and lower traffic emissions in Oslo. This interpretation is consistent with the higher correlation between ∑PAH and traffic markers in Catalonia (Jedynska et al., 2014).

The correlation between levoglucosan and $PM_{2.5}$, EC and OC was low to moderate. In the Flanders study, the patterns of average concentrations were also different for levoglucosan vs. EC, OC and $PM_{2.5}$ (Maenhout et al., 2012). The implication for epidemiological studies is that exposure to particles from wood burning and motorized traffic emission can be separated, provided that exposure can be assessed.

The K/levoglucosan ratio was comparable to previous studies (Puxbaum et al., 2007; Caseiro et al., 2009). The 0.3 ratio found in Oslo is consistent with wood combustion if fire places (Puxbaum et al., 2007) (Table S6).

### 4.5 LUR models

The explained variance of the developed levoglucosan LUR models was moderate (median $R^2$ = 60 %). That is only slightly lower than the $R^2$ for more frequently modeled pollutants like $PM_{2.5}$ or pollutants used as traffic markers – $NO_x$ or $PM_{2.5}$ absorbance,



which have mostly $R^2$ higher than 70 %. Recently LUR models for elemental composition of $PM_{2.5}$ and $PM_{10}$ were reported (de Hoogh et al., 2013). For elements representing traffic sources (Cu, Fe, Zn) models with high explained variances were found. Models for elements primarily related to non-traffic sources had more moderate explained variance. Median $R^2$ for LUR models for K in $PM_{2.5}$ was 41 % for the same four study areas, lower than for levoglucosan.

Information on the use of wood for heating in individual homes was not available in any of the four study areas. The three previous LUR studies of wood smoke also discussed the problem of obtaining good data on wood burning emissions (Su et al., 2009; Larson et al., 2007; Smargiassi et al., 2012). In the Seattle and Vancouver studies, neighborhood data from property databases was used (Su et al., 2009; Larson et al., 2007). Finer scale data was not reliable and the authors interpret their models as indicating which neighborhoods are more affected by wood smoke. In the Montreal study, chimney density was used as a proxy for wood burning (Smargiassi et al., 2012). Variables used in our models were unspecific for wood combustion emissions, but rather were associated with general human activity (negative direction natural variables) or describing population (population number or residential area). In Catalonia and Netherlands coordinates were also used in the models. In Catalonia levoglucosan levels were higher in Girona (located in the north) than in Barcelona. In the Netherlands higher concentrations were found in Groningen located in the northeast (Fig. S1). Interestingly, traffic related variables did not enter our models while LUR models for K (de Hoogh et al., 2013) in three study areas contained traffic related variables. This is consistent with the notion that levoglucosan is a more specific marker for wood combustion than K. In Oslo where levoglucosan correlated the highest with K, population density variable was used in models of both components. Despite the non-specific predictor variables, the structure of the models for at least the Netherlands and Catalonia differed from the models developed for other pollutants.

The three studies reporting LUR models for wood smoke concentrations also reported only moderate levels of explained variance – 57 % in Seattle (Su et al., 2008),

58 % in Vancouver (Larson et al., 2007; Su et al., 2008) and 0.40 for the global model in Montreal (Smargiassi et al., 2012). In the first two studies information about use of woodstove or houses with wood heating was available. In the model with the highest $R^2$ reported by Larson et al. wood smoke variables were not included. The $R^2$ of this model was 84 %. In the best model variables describing population and its social economic status were included. In the best model presented by Su et al. wood heating units variable as well as percentage of population in manufacturing trade were used. The Montreal model included a priori regional background $PM_{2.5}$, chimney density, wind speed, temperature and elevation in the model (Smargiassi et al., 2012). The previous model performances cannot be directly compared to our study, as the three North-American studies were based on mobile monitoring performed in winter evening hours only and averaged over routes or neighborhoods whereas we modeled averages of specific points based upon 14 day average samples including both daytime and nighttime. The studies in Vancouver and Montreal were furthermore based upon $PM_{2.5}$ monitoring using light scattering, which were assumed to primarily reflect wood burning emissions during the selected sampling conditions (Larson et al., 2007; Smargiassi et al., 2012).

The main limitation was the lack of variables describing specific sources of wood smoke e.g. information on wood installation of domestic heating systems. Another limitation of our study was the small number of sites available per study area for LUR model development. It has been reported that a small number of sites selected for LUR models development can cause overestimation of results of models validation used in our study (LOOCV) (Wang et al., 2013; Basagaña et al., 2012). But even with a limited amount of samples, the LUR models explained a substantial part of the spatial variation.



## 5 Conclusions

Substantial spatial contrasts were found within four study areas in levoglucosan concentrations but the differences between study areas were not statistically significant. Spatial variation patterns differed substantially from other measured pollutants including $PM_{2.5}$, $NO_2$ and EC, offering the potential to assess health effects of wood smoke separate from traffic-related air pollution. Levoglucosan correlated only moderately with K, another often used marker for wood smoke. Levoglucosan concentrations in the cold period were between 3 and 20 times higher compared to the warm period. The contribution of wood-smoke calculated based on levoglucosan measurements and previous European emission data to OC and $PM_{2.5}$ mass were 13 to 28 % and 3 to 9 % respectively in the full year. Larger contributions were calculated for the cold period. For four study areas LUR models for levoglucosan could be developed with a moderate explained variance (median adjusted $R^2$ = 60 %).

The advantage of our study was the standardization of every stage of the project. Samples were taken across Europe with the same equipment, analyzed in one laboratory and annual averages were calculated the same way and LUR models were developed centrally and according to standardized protocol. The LUR models of levoglucosan will be used to investigate a long-term health effects associated with biomass combustion processes in the coming future.

**The Supplement related to this article is available online at doi:10.5194/acpd-14-13491-2014-supplement.**

*Acknowledgements.* We would like to thank everybody involved in the project who participated in the air sampling, measurements, data management and the project supervision. The research leading to these results was funded by internal TNO funds and the European Community's Seventh Framework Program (FP7/2007-2011) projects ESCAPE (grant agreement 211250) and TRANSPHORM (ENV.2009.1.2.2.1).

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**Table 1.** Description of sampling campaign.

| Country | Study area | Sampling period | Sites | Site types | | |
|---|---|---|---|---|---|---|
| | | | | RB | UB | S |
| Norway | Oslo | 5 Feb 2009–29 Jan 2010 | 19 | 2 | 9 | 8 |
| the Netherlands | Rotterdam, Amsterdam, Groningen, Amersfoort | 17 Feb 2009–19 Feb 2010 | 16 | 4 | 4 | 8 |
| Germany | Munich/Augsburg | 1 Mar 2009–5 Nov 2009 | 20 | 5 | 6 | 9 |
| Spain | Catalonia (Barcelona, Girona, Sabadell) | 14 Feb 2009–14 Jan 2010 | 40 | 4 | 13 | 23 |

RB – regional background
UB – urban background
S – street site

**Table 2.** Mean, contrast, 25th, 75th percentiles of annual averages of levoglucosan for 4 European study areas.

| Study area | n | Mean [ng m$^{-3}$] | Minimum | Maximum | Range/ Mean [%] | Percentile 25th | 75th |
|---|---|---|---|---|---|---|---|
| Oslo | 19 | 86 | 10.0 | 285.0 | 321 | 42 | 106 |
| Netherlands | 16 | 70 | 29.0 | 122.0 | 133 | 42 | 95 |
| Munich/Augsburg | 20 | 102 | 27.0 | 218.0 | 187 | 76 | 119 |
| Catalonia | 40 | 64 | 3.0 | 362.0 | 562 | 19 | 87 |





**Table 3.** Spearman correlations between annual average concentrations of levoglucosan and other components.

| Country | $PM_{2.5}$ | $PM_{2.5}$ABS | $NO_x$ | EC | OC | ΣPAH | B[a]P | Σhopanes/ steranes | K |
|---|---|---|---|---|---|---|---|---|---|
| Oslo | 0.63** | 0.66** | 0.61** | 0.72** | 0.38 | 0.89** | 0.88** | 0.53* | 0.57* |
| Netherlands | 0.35 | −0.02 | −0.21 | −0.10 | 0.27 | 0.74** | 0.66** | −0.32 | 0.49 |
| Munich/Augsburg | −0.39 | −0.28 | −0.23 | −0.20 | −0.36 | 0.57** | 0.51* | −0.42 | −0.15 |
| Catalonia | −0.08 | −0.28 | −0.35* | −0.27 | 0.22 | 0.26 | 0.32* | −0.11 | 0.18 |
| Median | 0.13 | −0.15 | −0.22 | −0.15 | 0.24 | 0.65 | 0.58 | −0.22 | 0.33 |

* Significant correlation with $p < 0.05$
** Significant correlation with $p < 0.01$

**Table 4.** Calculated contribution of wood smoke to measured $PM_{2.5}$ OC and massCalculated according to Maenhout et al. (2012): OC from wood smoke = 5.59· levoglucosan, PM mass = 10.7· levoglucosan. Measured is mean concentrations from Jedynska et al. (2014) paper for OC and Eeftens et al. (2012) for $PM_{2.5}$ mass.

| | Levoglucosan ng m$^{-3}$ | Calculated OC wood smoke µg m$^{-3}$ | Calculated $PM_{2.5}$ wood smoke µg m$^{-3}$ | Measured OC µg m$^{-3}$ | Measured $PM_{2.5}$ µg m$^{-3}$ | Contribution wood smoke to OC % | Contribution wood smoke to $PM_{2.5}$ % |
|---|---|---|---|---|---|---|---|
| | Full year | | | | | | |
| Oslo | 86 | 0.48 | 0.92 | 1.70 | 8.60 | 28.3 | 10.7 |
| Netherlands | 70 | 0.39 | 0.75 | 1.80 | 17.30 | 21.7 | 4.3 |
| Munich/Augsburg | 102 | 0.57 | 1.09 | 2.70 | 14.30 | 21.1 | 7.6 |
| Catalonia | 64 | 0.36 | 0.68 | 2.80 | 15.60 | 12.8 | 4.4 |
| | Warm period | | | | | | |
| Oslo | 15 | 0.08 | 0.16 | 1.01 | 7.30 | 8.2 | 2.2 |
| Netherlands | 38 | 0.21 | 0.40 | 1.72 | 16.40 | 12.2 | 2.4 |
| Munich/Augsburg | 48 | 0.27 | 0.51 | 1.87 | 11.30 | 14.3 | 4.5 |
| Catalonia | 16 | 0.09 | 0.17 | 2.01 | 14.80 | 4.5 | 1.2 |
| | Cold period | | | | | | |
| Oslo | 294 | 1.64 | 3.15 | 2.13 | 11.10 | 77.2 | 28.3 |
| Netherlands | 120 | 0.67 | 1.29 | 1.96 | 17.60 | 34.3 | 7.3 |
| Munich/Augsburg | 144 | 0.80 | 1.54 | 1.56 | 12.80 | 51.6 | 12.0 |
| Catalonia | 152 | 0.85 | 1.63 | 3.50 | 17.40 | 24.3 | 9.4 |



**Table 5.** Description of LUR models for levoglucosan.

| Study area | LUR model | $n$ | $R^2$ | LOOCV $R^2$ | RMSE |
|---|---|---|---|---|---|
| Oslo | 22.59 + 0.01955· POP1000 | 19 | 0.59 | 0.39 | 40.46 |
| Netherlands | 22.72 – 0.00005213 · NATURAL_1000 + 0.0003478 · xcoord | 16 | 0.60 | 0.48 | 20.75 |
| Munich/Augsburg | 74.88 + 148.42 · HD_LD_RES_300 – 651.46 · URBGREEN – 298.69 · NATURAL1000 | 20 | 0.60 | 0.36 | 27.69 |
| Catalonia | –3998.2 – 0.00000617 · URBGREEN_5000 – 2.92 · SQRALT + 0.000885 · ycoord | 38 | 0.71 | 0.62 | 20.27 |
| Median | | | 0.60 | 0.44 | 24.22 |

POP1000 – population I the buffer of 1000 m
NATURAL_1000 – natural land in the buffer of 1000 m
HD_LD_RES_300 – all residential land in the buffer of 300 m from a sampling site
URBGREEN_5000 – urban green space in the buffer of 5000 m from a sampling site
SQRALT – the square root of altitude
xcoord – X coordinate, which indicates (+)increased, (–)decreased trends of air pollution along the x-axis direction
ycoord – Y coordinate, which indicates (+)increased, (–)decreased trends of air pollution along the y-axis direction

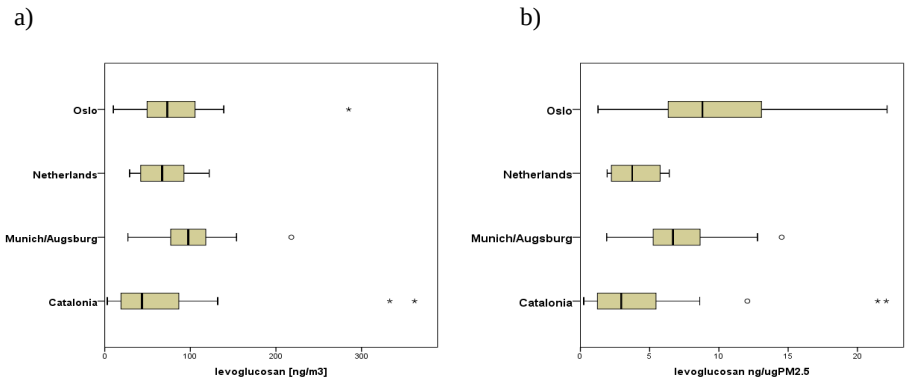


**Figure 1.** Distribution of the adjusted annual average concentration of levoglucosan within study areas. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. **(a)** results in ng $m^{-3}$, **(b)** results in ng $(\mu g\ PM_{2.5})^{-1}$.





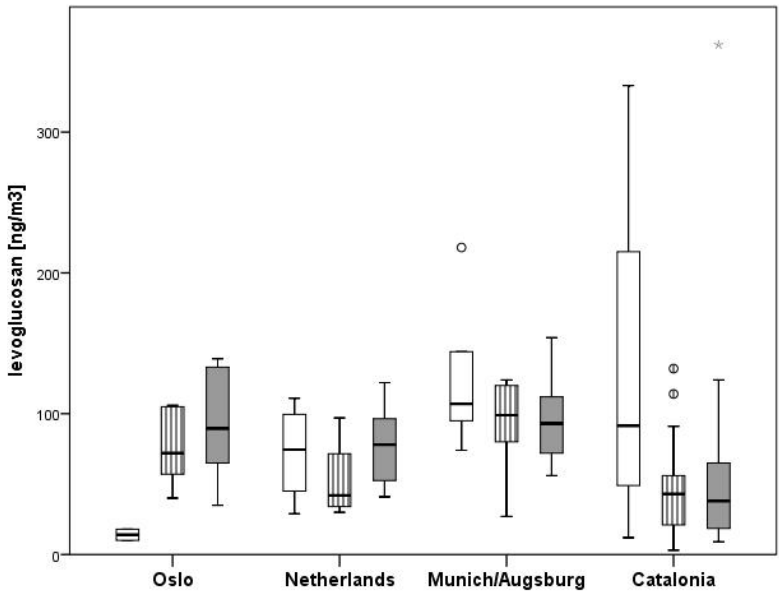


**Figure 2.** The adjusted annual average concentration of levoglucosan for different site types. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. White – regional background, striped – urban background, grey – street locations.

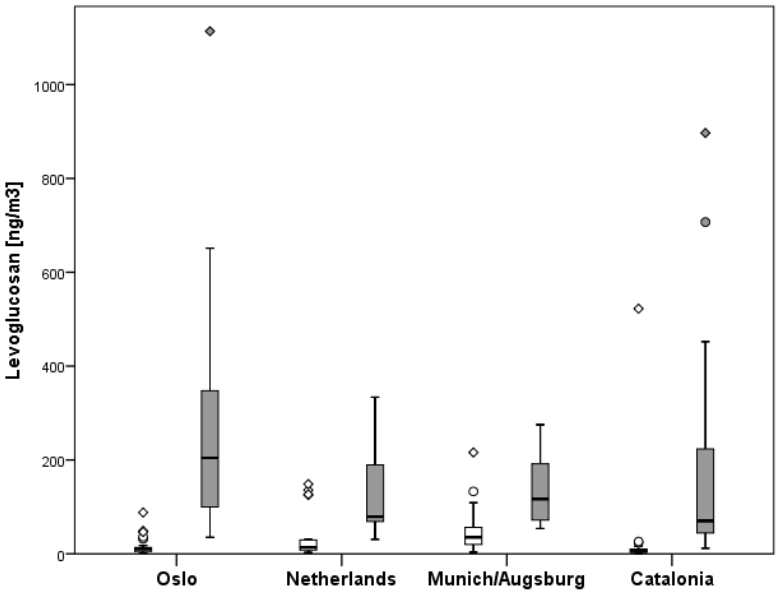


**Figure 3.** Seasonal differences of levoglucosan concentrations. White – warm, grey – cold season.