Spatial variations of levoglucosan in four European study areas

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Highlights:

- A wood burning marker – levoglucosan – was measured in four study areas across Europe
- Much larger within than between study area contrast in levoglucosan concentration was found.
- Levoglucosan concentrations in the cold (heating) period were between 3 and 20 times higher compared to the warm period.

Abstract

Relatively little is known about long term effects of wood smoke on population health. A wood combustion marker – levoglucosan – was measured using a standardized sampling and measurement method in four European study areas (Oslo, The Netherlands, Munich/Augsburg, Catalonia) to assess within and between study area spatial variation. Levoglucosan was analyzed in addition to: PM2.5, PM2.5 absorbance, PM10, polycyclic aromatic hydrocarbons (PAH), nitrogen oxides (NOx), 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 reference site. Land use regression (LUR) models were developed to explain the spatial variation of levoglucosan. Much larger within than between study area contrast in levoglucosan concentration was found. Spatial variation patterns differed from other measured pollutants: PM2.5, NOx and EC. Levoglucosan had the highest spatial correlation with ΣPAH (r=0.65) and the lowest with traffic markers – NOx, Σhopanes/steranes (r = -0.22). 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 PM2.5 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%. The LUR models included population and natural land related variables. In conclusion, substantial spatial variability was found in levoglucosan concentrations within study areas. Wood smoke contributed substantially to especially wintertime $PM_{2.5}$ OC and mass. The low to moderate correlation with PM2.5 mass and traffic

68 markers offers the potential to assess health effects of wood smoke separate from traffic-related air

69 pollution.

70 Keywords:
71 Levoglucosan, EC, OC, PAH, LUR, PM2.5, Spatial variation
72 [1]

[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; NOx, nitrogen oxides; NO2, nitrogen dioxide; PM2.5, mass concentration of particles less than 2.5 mm in size; PM2.5 absorbance, measurement of the blackness of PM2.5 filters, this is a proxy for elemental carbon, which is the dominant light absorbing substance; PM10, mass concentration of particles less than 10 mm in size; RB, regional background; S, Street; EPA, United States Environmental Protection Agency; LUR, Land Use Regression; RMSE, Root Mean Squared Error.

1. Introduction

Human exposure to air pollution has been associated with a range of health effects (Brunekreef, Holgate 2002, Pope, Dockery 2006). Particle matter (PM) with diameters smaller than 10 or 2.5 µm (PM10, PM2.5, 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, 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 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 in particular 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, 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, 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 of levoglucosan levels in these different studies 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 PM2.5, PM10 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 PM2.5 and PM1 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: NOx, NO_2, PM2.5, PM10, PM2.5 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, de Hoogh et al. 2013, Eeftens et al. 2012b, 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 PM2.5. mass, other organic components, another biomass combustion 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).

Table 1. Description of sampling campaign

Country	Study area	Sampling period	Sites	Site types		
				RB	UB	S
Norway	Oslo	05.02.2009 – 29.01.2010	19	2	9	8
The Netherlands	Rotterdam, Amsterdam, Groningen, Amersfoort	17.02.2009 – 19.02.2010	16	4	4	8
Germany	Munich/Augsburg	01.03.2009 – 05.11.2009	20	5	6	9
Spain	Catalonia (Barcelona, Girona, Sabadell)	14.01.2009 – 14.01.2010	40	4	13	23

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

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 PM2.5 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 3.000 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.

2.3Analytical 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. (Simpson et al. 2004). Briefly, each filter was extracted in ethylacetate with 0.5% triethylamine in an ultrasonic bath for 1 hour. 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 expanded uncertainty (U) amounts 30%. Expanded uncertainty was calculated as 2 times the uncertainty (U_c) incorporating reproducibility (vc, recovery (u_{tv}) and accuracy of the calibration standard (u_j), following the Dutch norm NEN 7777 Environment - Performance characteristics of measurement methods ($U_c = \sqrt{((vc)^2+(u_j)^2+(u_{tv})^2)}$). Reproducibility of our method is between 7 and 15 % depending on levoglucosan concentration in analysed samples.

2.3.2 EC/OC, PAH, hopanes, steranes, PM2.5, NO_2 and elemental composition

Analytical and sampling methods and spatial variability across Europe of PM2.5, 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. (Jedynska et al. 2014). In summary, 1cm^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).

PM2.5 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.

PM2.5 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 25^{th} and 75^{th} 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

246 winter. We also analyzed differences based on all individual measurements divided into the warm
247 (April – September) and cold period (October – March).
248 The contribution of wood smoke to the measured OC and PM2.5 was calculated by using
249 previously published conversion factors from levoglucosan to OC and mass in wood smoke
250 (Puxbaum et al. 2007; Maenhaut et al. 2012; Caseiro et al. 2009). We used factors of 5.59 and 10.7
251 to calculate wood smoke OC and wood smoke mass respectively (Maenhaut et al. 2012). These
252 factors have been derived from emission testing in Austria and may be different elsewhere in
253 Europe. The levoglucosan content of wood smoke depends on the type of wood burnt (soft or hard
254 wood), temperature and type of burning process. The estimated uncertainty in levoglucosan content
255 has been estimated to be about 30% (Maenhaut et al. 2012).
256

257 ## 2.6 Adjustment for temporal variability

258
259 The three two-week samples were used to estimate the annual average level of levoglucosan.
260 For practical reasons, it was not possible to collect samples simultaneously at all sites of each study
261 areas. Due to temporal variation in air quality, the simple average from the concentrations in the
262 three sampling periods at the sampling sites could reflect both spatial and temporal variation. In
263 order to correct for temporal variation, a reference site was continuously measured in each study
264 area during a full year including the sampling period. The reference site was located at a
265 background location, away from local emissions. Our correction procedure followed the modified
266 ESCAPE procedure used for EC/ OC, PAH and hopanes/steranes (Eeftens et al. 2012b, Cyrys et al.
267 2012).
268 At the reference sites, the following components were measured: NOx, NO_2, PM2.5, PM2.5
269 absorbance and PM10. Levoglucosan and EC/ OC, PAH and hopanes/steranes were not analyzed at
270 the reference sites because of lack of sampling equipment. To adjust for temporal variation, we
271 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 PM2.5, PM2.5 absorbance, PM10 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 90m 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.

Data for wood smoke emission was also used as variables. Emission data of PM2.5, EC, OC, B[a]P originating from wood smoke was obtained in the framework of three European projects: European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions (EUCAARI) (https://www.atm.helsinki.fi/eucaari/), Monitoring Atmospheric Composition and Climate (MACC) (https://www.gmes-atmosphere.eu/) and TRANSPHORM (www.transphorm.eu). The data was available for grids of 7 x7 km for all four study areas and additionally in The Netherlands in the grid of 1 x 1km (Kuenen et al. 2014).

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 section 3.2 which shows seasonal variation. . In the online supplement Table S2 the components selected for temporal adjustment of levoglucosan concentrations are presented. In all study areas NOx correlated highest with levoglucosan. NOx was used for temporal adjustment in the Netherlands, Munich/Augsburg and Catalonia. In Oslo, due to an incomplete data set of NOx at the reference site, we used PM2.5 absorbance for temporal adjustment. The correlation between levoglucosan and PM2.5 absorbance was only slightly lower than between levoglucosan and NOx (r=0.984 vs 0.997). Correlations ranged between 0.98 and 0.99 (Table S2), 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 Figure 1 and Table 2. Differences between site types are presented in Figure 2 and in supplement (Table S4).

3.1Within and between study area contrast

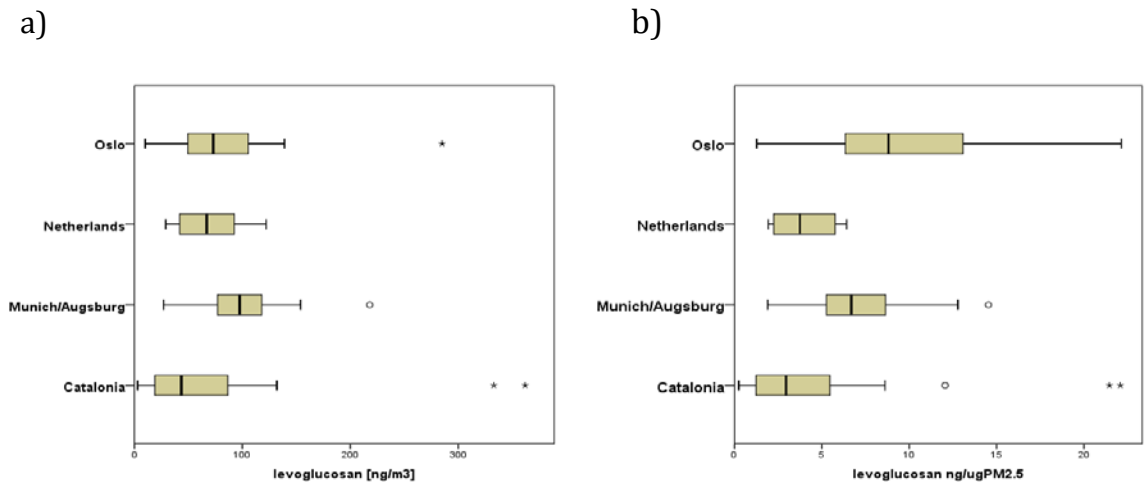

Figure 1. Distribution of the adjusted annual average concentration of levoglucosan within study areas. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. a) results in ng/m^3, b) results in ng/µgPM2.5.

346 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

347
348

349 Levoglucosan concentrations were highest in Munich/Augsburg – 102 ng/m^3 and lowest in
350 Catalonia 64ng/m^3 (Figure 1, Table 2) but the differences in levoglucosan concentrations between
351 study areas were not statistically significant. The lack of samples taken in winter (December –
352 February) in Munich /Augsburg may have influenced the annual average concentrations. Because of
353 the applied correction of the concentrations for temporal variation using a continuous site, the
354 impact is diminished. To the extent that the seasonal pattern of NO_x (used for correction) and
355 levoglucosan differ, correction may not be sufficient. To test this, we deleted the winter samples
356 from the Netherlands and observed that the temporally adjusted annual average changed from 70 to
357 60 ng/m^3.
358 There was high within study area variation. In the Netherlands range to mean ratio was 132% and in
359 Catalonia the ratio was the highest – 562% (Table 2). In Catalonia two outliers were identified: one
360 at a street location in Barcelona with only two measurements, both taken in the colder part of the
361 year with high levoglucosan concentrations. The second outlier was a regional background site in
362 Girona with two out of three very high concentrations of levoglucosan measured in February and
363 November. In Oslo an urban background site was identified as an outlier due to extremely high
364 concentration found in the sample taken in November. In Munich/Augsburg a regional background
365 site situated in the small town Erding was detected as an outlier due to very high levoglucosan
366 concentration in the summer sample.
367 In Catalonia levoglucosan levels were higher in the Girona area than in Barcelona and Sabadell
368 (Figure S1). In the Netherlands the highest concentrations were found in the Groningen area and the

lowest in the Rotterdam (Figure S1). These spatial patterns were opposite to the patterns observed for traffic-related pollutants.

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

There are significant differences between levels of levoglucosan fraction in PM2.5. The highest fraction of levoglucosan in PM2.5 was found in Oslo (9.51 ng/µgPM2.5) (Figure1b). 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 PM2.5 but was not a statistical outlier.

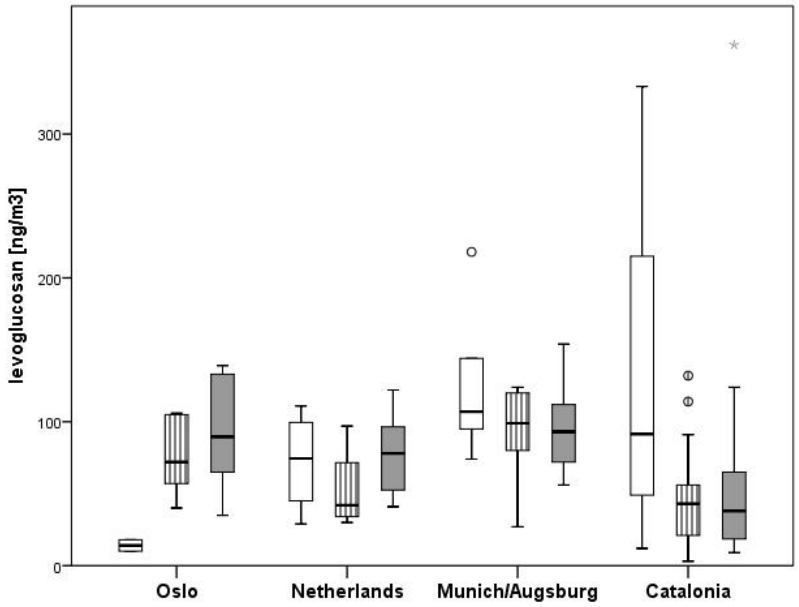

Figure 2. The adjusted annual average concentration of levoglucosan for different site types. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. White – regional background, striped – urban background, grey – street locations.

3.2 Seasonal differences

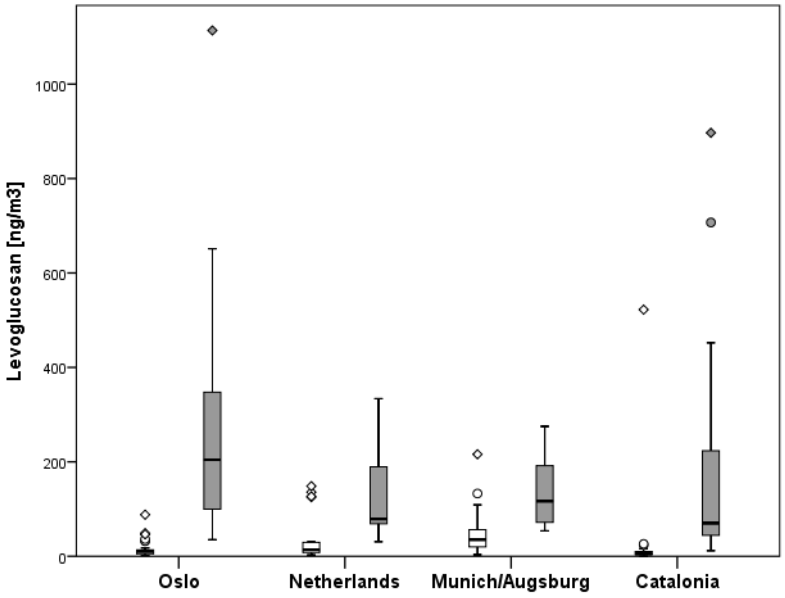

Figure 3. Seasonal differences of levoglucosan concentrations. White – warm, grey – cold season.

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 (Figure 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 (Figure 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 PM2.5 and levoglucosan (median r=0.33). The correlation between K in PM10 and levoglucosan was even slightly lower (median r= 0.27).

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

Country	PM2.5	PM2.5ABS	NOx	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

3.4Contribution of wood smoke to OC and PM2.5 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 PM2.5 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.

Table 4. Calculated contribution of wood smoke to measured PM2.5 OC and massCalculated according to Maenhaut 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 PM2.5 mass.

	Levoglucosan	Calculated OC wood smoke	Calculated PM2.5 wood smoke	Measured OC	Measured PM2.5	Contribution wood smoke to OC	Contribution wood smoke to PM2.5
	ng/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	%	%
	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

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 $p > 0.05$). Wood smoke emission data did not enter the final models, possibly due to insufficient spatial resolution or quality of the data.

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 1000m
NATURAL_1000 – natural land in the buffer of 1000m
HD_LD_RES_300 – all residential land in the buffer of 300m from a sampling site
URBGREEN_5000 – urban green space in the buffer of 5000m 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

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 traffic-related pollutants such as PM2.5, NO2 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 PM2.5 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, PM2,5abs, EC, ∑hopanes/steranes) and PM2.5 mass which had the highest concentrations in

475 Barcelona (and other southern European areas) and the lowest concentrations in Oslo (and other
476 Northern European areas) (Cyrys et al. 2012, Eeftens et al. 2012c). PAH concentration also had
477 similar levels in southern and northern Europe (Jedynska et al. 2014). In the cold period,
478 levoglucosan concentrations were about two times higher in Oslo than in the other three study areas,
479 consistent with the expected use of wood for heating. Although in general levoglucosan
480 concentrations tend to be higher in Northern Europe a review table of published studies showed that
481 this was not consistently found (Reche et al. 2012). Higher levoglucosan concentrations may occur
482 outside Oslo and other major North-European cities where wood is more often used. High
483 wintertime levoglucosan concentrations (900 ng/m^3) have indeed been reported for the small town
484 of Lycksele in Northern Sweden (Reche et al. 2012).
485
486 The large variability in average levoglucosan concentrations in our study is consistent with
487 previously reported substantial differences in levoglucosan for different sites in Europe (Reche et al.
488 2012). The comparison is limited as studies differ widely in season of measurements, often winter,
489 one winter month or forest burning periods (Caseiro, Oliveira 2012, Reche et al. 2012, Pio et al.
490 2008). Studies further differ in location, ranging from large urban areas to high altitude sites. Few
491 studies have compared concentrations across countries. Puxbaum et al. reported annual
492 levoglucosan average concentration for six rural background site across Europe (Puxbaum et al.
493 2007). The concentrations varied from 5.2 ng/m^3 in the Azores to 309 ng/m^3 in Hungary. A study at
494 7 urban and rural sites in Flanders reported annual median concentrations between 69 and 95 ng/m^3
495 for five sites (Maenhaut et a. 2012), very comparable to our findings. Very high correlations of
496 daily values at these sites were found, explained by the importance of regional wood burning and
497 increased burning of wood on the same (cold, winter) days at all sites (Maenhaut et al. 2012). At
498 one coastal site the annual median was 34 ng/m^3 related to more impact of cleaner maritime air. At
499 the site selected specifically to have wood burning in homes near the site, the median was 200
500 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 (section 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 et al. 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). The ratio for Munich/Augsburg is likely influenced by absence of samples taken in the coldest months (December – February). Seasonal variation of levoglucosan in Augsburg was previously presented by Pietrogrande et al. (Pietrogrande et al. 2011). Reported winter/summer ratio was 3, similarly as in our study. But winter samples were taken from mid-February to mid-March which is not representative for the coldest months. In the Austrian study, winter/ summer ratios of 6-8 were found. In Flanders, much higher winter/summer ratios (~30) were reported (Maenhaut 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 (Maenhaut et al. 2012).

4.3 Contribution of wood smoke to OC and PM mass

Our calculated contribution of wood smoke to measured OC and PM2.5 mass compares well with previous studies. A study in three Austrian regions reported wood smoke contributions to OC and PM10 mass of 18 - 38% to OC and 5 – 13 % to PM10 mass for annual averages (Caseiro et al. 2009). The wood smoke contribution increased to 31-70% and 7-20% for winter OC and PM10 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 PM10 mass of 20 - 36% to OC and 5 – 13 % to PM10 mass for annual averages (Maenhaut et al. 2012). The wood smoke contribution increased to 36-60% and 9-22% for winter OC and PM10 mass averages. The conversion factor used in our study assumes that mostly softwood (e.g. spruce) is burnt (Maenhaut 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 PM10 limit value was even higher than the contribution to the winter average (Maenhaut et al. 2012).

4.4 Correlation with other components

We found a relatively low spatial correlation between levoglucosan and potassium (K) in PM2.5. 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.

565 2008; Puxbaum et al. 2007; Caseiro et al. 2009; Reche et al. 2012). Other sources of K are soil,
566 seawater, meat cooking and waste incinerators (Giannoni et al. 2012, Urban et al. 2012).
567 Furthermore, we measured total K using XRF whereas only the fraction of water soluble K is
568 considered as a tracer for wood smoke (Pio et al. 2008). Finally, the relatively low spatial variation
569 of potassium within study areas, especially has contributed to low correlation with levoglucosan.
570 Our study suggests that care is needed to interpret spatial variation of K as reflecting wood burning
571 emissions.
572
573 The highest correlation was found between levoglucosan and ∑PAH and B[a]P (0.51 – 0.89). Wood
574 burning is known to be one of the PAH sources (Ravindra, Sokhi & Van Grieken 2008) The
575 correlation with ΣPAH was highest in Oslo and lowest in Catalonia, probably related a combination
576 of higher wood smoke emissions and lower traffic emissions in Oslo. This interpretation is
577 consistent with the higher correlation between ∑PAH and traffic markers in Catalonia (Jedynska et
578 al. 2014).
579
580 The correlation between levoglucosan and PM2.5, EC and OC was low to moderate. In the Flanders
581 study, the patterns of average concentrations were also different for levoglucosan versus EC, OC
582 and PM2.5 (Maenhaut et al. 2012). The implication for epidemiological studies is that exposure to
583 particles from wood burning and motorized traffic emission can be separated, provided that
584 exposure can be assessed.
585
586 The K/levoglucosan ratio was comparable to previous studies (Puxbaum et al. 2007; Caseiro et al.
587 2009). The 0.3 ratio found in Oslo is consistent with wood combustion in fire places (Puxbaum et
588 al. 2007) (Table S6).
589

4.5LUR 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 PM2.5 or pollutants used as traffic markers – NO_x or PM2.5 absorbance, which have mostly R^2 higher than 70%. Recently LUR models for elemental composition of PM2.5 and PM10 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 PM2.5 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 (Figure 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 PM2.5, 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 PM2.5 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).

641 But even with a limited amount of samples, the LUR models explained a substantial part of the
642 spatial variation.
643
644 ## 5. Conclusions
645
646 Substantial spatial contrasts were found within four study areas in levoglucosan concentrations but
647 the differences between study areas were not statistically significant. Spatial variation patterns
648 differed substantially from other measured pollutants including PM2.5, NO2 and EC, offering the
649 potential to assess health effects of wood smoke separate from traffic-related air pollution.
650 Levoglucosan correlated only moderately with K, another often used marker for wood smoke.
651 Levoglucosan concentrations in the cold period were between 3 and 20 times higher compared to
652 the warm period. The contribution of wood-smoke calculated based on levoglucosan measurements
653 and previous European emission data to OC and PM2.5 mass were 13 to 28% and 3 to 9%
654 respectively in the full year. Larger contributions were calculated for the cold period. For four study
655 areas LUR models for levoglucosan could be developed with a moderate explained variance
656 (median adjusted R^2 = 60%).
657
658 The advantage of our study was the standardization of every stage of the project. Samples were
659 taken across Europe with the same equipment, analyzed in one laboratory and annual averages were
660 calculated the same way and LUR models were developed centrally and according to standardized
661 protocol. The LUR models of levoglucosan will be used to investigate a long-term health effects
662 associated with biomass combustion processes in the coming future.
663
664
665
666

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