

**Spatial variations and development of land use
regression models of PAH, EC/OC, levoglucosan and
oxidative potential of PM_{2.5} in European study areas**

Aleksandra Jedyńska

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Spatial variations and development of land use regression models of PAH, EC/OC, levoglucosan and oxidative potential of PM2.5 in European study areas

Ruimtelijke variatie en de ontwikkeling van land use regressie modellen van PAK, EC/OC, levoglucosan en oxidatieve potentieel van PM2.5 in Europese studie gebieden

(met een samenvatting in het Nederlands)

Proefschrift

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Aleksandra Dorota Jedyńska

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Łódź, Polen

Promotor:

Prof. dr. ir. B. Brunekreef

Copromotoren:

Dr. ir. I.M. Kooter

Dr. ir. G. Hoek

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Chapter 1

General introduction

It has been shown that human exposure to air pollution causes adverse health effects (Brunekreef, Holgate 2002, Pope, Dockery 2006). The most used indicator of air quality is the concentration of particulate matter with diameters smaller than 10 or 2.5 μm (PM₁₀, PM_{2.5}, respectively). 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). Most studies of PM composition have investigated short term health effects caused. In Europe, recently the ESCAPE project contributed significantly to development of knowledge on long term adverse health effect of PM elemental constituents (Eeftens et al. 2014, Fuertes et al. 2014, Wang et al. 2014, Beelen et al. 2015). But still there is little knowledge about long term adverse health effects caused by exposure to organic PM components.

Recently, several papers were published which reviewed the current knowledge on adverse health effects of PM composition or pollution with from specific sources (Naeher et al. 2007, Kim et al. 2013, WHO 2013).

PM organic markers

There are thousands of organic components in the particulate and gas phase of ambient air. Characterizing exposure to all individual components is not feasible. An approach, which has been used in some studies, is to quantify **elemental (EC) and organic carbon (OC)** as more generic indicators of air quality. EC is a highly polymerized dark fraction which is resistant to oxidation at temperatures below 400°C (Penner, Novakov 1996). The surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes. EC is emitted primarily by motorized traffic particularly diesel emissions and combustion of coal and wood. EC correlates highly with black smoke (BS), black carbon (BC) and PM absorbance (Cyrus et al. 2003, Heal, Quincey 2012, Schaap, Denier van der Gon 2007, Keuken et al. 2012). OC is a mixture of organic compounds such as aliphatic and aromatic hydrocarbons, acids, etc. Differentiation of elemental and organic carbon is usually achieved via assessment of various thermal, optical and chemical parameters. OC can be distinguished into primary and secondary OC. Secondary OC is formed in the atmosphere from volatile and semi-volatile organic components.

Polycyclic aromatic hydrocarbons (PAH) are persistent organic components associated with various adverse health effects (Ravindra, Sokhi & Van Grieken 2008). The EU limits the annual average of Benzo[a]pyrene (B[a]P) as a proxy for all PAH in ambient air to 1 ng/m³ (EU Directive 2004/107/EC). PAH are mostly formed during incomplete combustion processes. Sources include: domestic, transportation, industrial, and agricultural processes. Domestic emissions arise from burning wood, coal, oil and garbage for heat and waste disposal. Road and

maritime transportation can be significant sources of PAH although levels depend on engine type and age, and fuel used. Industrial PAH emissions originate mainly from metal and steel production, the petrochemical industry and power generation. PAH from agriculture derive mainly from open biomass burning (Ravindra et al. 2008). There are 16 PAHs, known as priority PAHs of the United States Environmental Protection Agency (US EPA), which are often the focus of environmental studies of air quality. The 16 EPA priority PAHs are from 2 to 6 benzene rings: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[ah]anthracene, indeno[123-cd] pyrene, benzo[ghi]perylene.

Hopanes and steranes are components present in crude oil. They have been used as markers for motor vehicle exhaust particles in the atmosphere (Simoneit 1999). Hopanes and steranes are also present in lubricating oil used by both gasoline- and diesel-powered motor vehicles, and are also found in diesel fuel (Cass 1998). Hopanes and steranes have been associated with lung toxicity (McDonald et al. 2004), but have not been used as exposure metrics in epidemiological studies so far.

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 the 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). Biomass combustion is an important source of ambient particle matter and carbonaceous aerosol (Naehler et al. 2007). The most important sources of wood smoke are indoor cooking, forest fires, agricultural burning and in particular residential heating by fireplaces and woodstoves (Chafe et al. 2015).

Oxidative potential (OP) of PM has been suggested as a health relevant parameter for epidemiological studies. Oxidative potential is defined as a measure of the capacity of PM to oxidize specific target molecules. Because OP level integrates various PM characteristics (e.g. size, chemical composition, biological properties, surface) it might be a more health relevant PM metric than PM mass or single PM compound (Boogaard et al. 2012, Borm et al. 2007). However, few epidemiological studies have evaluated whether OP of PM predicts health effects better than PM mass. Little is known about the spatial variation of oxidative potential, which is needed to assess whether OP of PM predicts health effects related to long-term exposure better than PM_{2.5} or components within PM_{2.5}. Several chemical assays exist to assess the oxidative potential of PM. They differ from each other in sensitivity to the reactive oxygen species (ROS) generating compounds and analytical method (Ayres et al. 2008). A well-known assay is based on the consumption of dithiothreitol (DTT) related to the ability of redox

active compounds to transfer electrons from DTT to oxygen (Cho et al. 2005, Kumagai et al. 2002). The DTT assay is especially sensitive to organic components such as quinones. Another assay is based on triggering of acridinium ester by reductive chemiluminescent (CRAT). With this assay the amount of formed H₂O₂ is determined (Zomer et al. 2011). The assay is especially sensitive to oxidants such as ferric or cupric ions or organic species (e.g. quinones). Few studies compared the different OP assays (Janssen et al. 2014, Yang et al. 2014, Kunzli et al. 2006) showing only moderate correlations between assays, likely caused by their sensitivity to different PM compounds.

Land use regression models

Land use regression (LUR) models are used to explain the measured spatial variation of the concentration of a pollutant by geographic predictor variables such as elevation, traffic density, road networks and industrial land use. These models are then used as a tool for exposure assessment in epidemiological studies (Hoek et al. 2008). LUR models have been shown to be a cost-effective method to explain the spatial variation in air pollution in a number of studies (Beelen et al. 2013). Most modeled pollutants are PM_{2.5}, PM₁₀ and compounds strongly affected by traffic (NO_x, PM absorbance, EC) (Beelen et al. 2013, Eeftens et al. 2012). Few LUR models have been developed for pollutants for which traffic is not a major source. Recently, LUR models were developed for the elemental composition of PM_{2.5} and PM₁₀ in 20 European study areas (de Hoogh et al. 2013, de Hoogh et al. 2013). Within the framework of NPACT, LUR models for EC and OC were developed (Vedal et al. 2013). LUR models for PAH concentrations were developed in an American study (Noth et al. 2011). Other three North American studies presented a LUR for markers of wood smoke (Larson et al. 2007, Su et al. 2008, Smargiassi et al. 2012).

ESCAPE and TRANSPHORM projects

ESCAPE (European Study of Cohorts for Air Pollution Effects) and TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) are EU FP7 funded projects designed to provide advanced knowledge on the impact of transport emissions and outdoor air pollution on human health in Europe. In selected European locations both projects added air pollution exposure assessment to health data available from various European cohort studies. The ESCAPE epidemiological study focused on four categories of adverse health effects:

- Pregnancy outcomes and children's respiratory and allergic outcomes
- Respiratory morbidity
- Cardiovascular morbidity

- Mortality outcomes and cancer incidence.

In the framework of the ESCAPE project, 36 study areas were used to assess concentrations of NO_x and NO_2 across Europe. In 20 of those study areas $\text{PM}_{2.5}$, PM_{10} , $\text{PM}_{2.5}$ absorbance and elemental composition were additionally measured. For this thesis, further $\text{PM}_{2.5}$ characterization was conducted in ten of the ESCAPE study areas. Specifically the concentrations of atmospheric EC/OC, PAH and oxidative potential were determined. In four of these ten study areas, hopanes/steranes and levoglucosan were additionally analyzed.

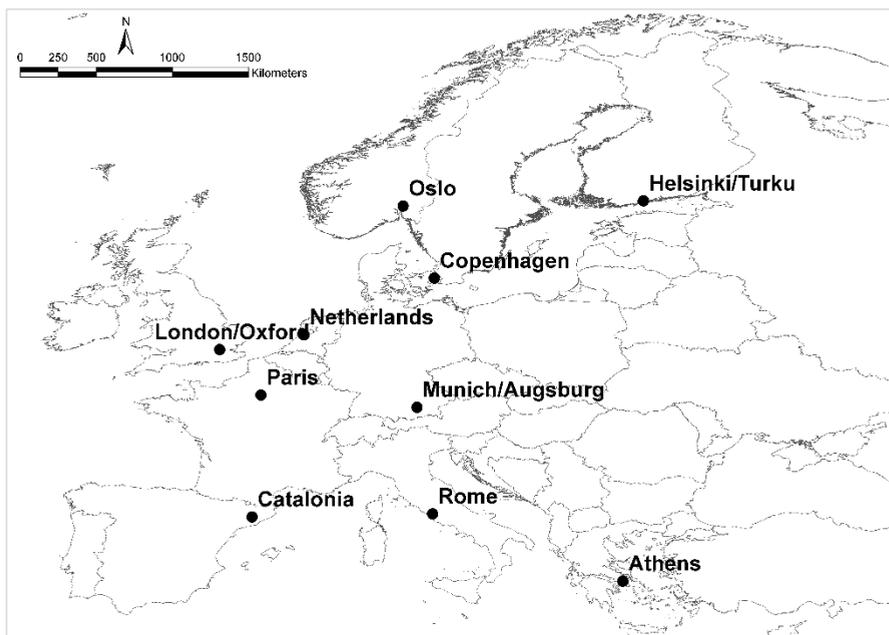


Figure 1. European study areas from which the data for this thesis were obtained

Thesis aims

The thesis was developed in the framework of the ESCAPE and THRANSFORM projects. The goals of the thesis were:

- Determination of the spatial contrast of the ambient concentration of specific organic components (EC/OC, PAH and hopanes/steranes, levoglucosan) and oxidative potential within and between European study areas.
- Assessment of the relationship between those components with other components measured within the ESCAPE project (NO_2 , NO_x , $\text{PM}_{2.5}$ mass and absorbance).
- Development and evaluation of LUR models for EC, OC, PAH and hopanes/steranes, levoglucosan and oxidative potential.

- Assessment of the correlation of the predictions of the developed models with the predictions of the earlier published models for PM_{2.5} and PM_{2.5} absorbance.

Thesis outline

In **chapter 2** the spatial variations of EC/OC, PAH and hopanes/steranes between and within 10 European study areas are presented. We also assessed the spatial relationship between those components and NO_x, NO₂, PM_{2.5} mass and absorbance. In **chapter 3** development and evaluation of LUR models for EC/OC, PAH and hopanes/steranes in 10 study areas is described. To evaluate the added value of the models, the predictions of the models were compared with prediction of previously developed PM_{2.5} mass and absorbance models. In **chapter 4** spatial variation of the wood smoke marker levoglucosan between and within four study areas is presented. We determined the contribution of wood smoke to fine particle OC and mass. Further, we presented the relationship between levoglucosan and PM_{2.5} mass, other organic components, another biomass combustion marker – potassium (K). Finally, we developed and evaluated LUR models of levoglucosan. In **chapter 5** we present the spatial variation of oxidative potential between and within study areas. We determined oxidative potential with two different assays. In ten study areas we applied the DTT assay and in four of these ten study areas we added the CRAT-ROS assay. For both assays LUR models were developed. **Chapter 6** consists of discussion of the main findings of this thesis, including potential implications for routine monitoring networks and modeling of PM composition and recommended improvement for future modeling studies.

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Chapter 2

Spatial variations of PAH, hopanes/steranes and EC/OC concentrations within and between European study areas

Aleksandra Jedynska
Josef Cyrus
Rob Beelen
Marta Cirach
Christian Madse
Klea Katsouyanni
Kees Meliefste
Arto Pennanen
Ingeborg M. Kooter

Gerard Hoek
Menno Keuken
Giulia Cesaroni
Kees de Hoogh
Christophe Declercq
Helgah Akhlaghi Makarem
Mark Nieuwenhuijsen
Ole Raaschou-Nielsen

Marloes Eeftens
Christophe Ampe
Francesco Forastiere
Audrey De Nazelle
Kirsten T. Eriksen
Timo Lanki
Marieke Oldenwening
Bert Brunekreef

Abstract

Limited information is available on the contribution of organic components in particulate matter to health effects related to fine particles. Spatial variability of specific fine particle organic components has not been assessed with consistent methods. The aim of this paper is to assess spatial variation of organic components of fine particles within and between European study areas. Highly standardized measurements of polycyclic aromatic hydrocarbons (PAH), hopanes/steranes, elemental/organic carbon (EC/OC) and levoglucosan were performed measured in ten study areas across Europe. In each study area, measurements were conducted at street, urban and regional background sites. Three two-week samples were taken per site and the annual average levels of pollutants were calculated using continuous measurements at one background site as a reference.

Substantial variations within and between the study areas were found. EC/OC and hopanes/steranes concentrations were highest in southern European study areas and lowest in northern locations. PAH concentrations were lowest in London/Oxford and highest in Copenhagen, Rome and Athens. Concentrations at street locations were higher than at background locations in all study areas and for all components. However, these differences varied considerably between study areas and components. EC had the highest median street to urban background ratio (1.62), OC the lowest (1.32). EC was highly correlated with NO_x and $\text{PM}_{2.5}$ absorbance in all areas, with median $r = 0.85$ and $r = 0.89$, respectively. The correlation between OC and other components was variable, with a median correlation of 0.65 with $\text{PM}_{2.5}$ mass and a weak (0.18) correlation with Σ hopanes/steranes. Σ PAH correlated moderately with EC ($r = 0.59$) and weakly with Σ hopanes/steranes ($r = 0.36$).

In conclusion, substantial variability was found in spatial patterns of atmospheric EC, OC, PAH and hopanes/steranes both within and between European study areas. The application of this highly standardized measurement approach across different locations will contribute to a consistent assessment of air pollutant levels and potentially contribute to understanding health effects associated with them.

Introduction

It has been shown that human exposure to air pollution causes adverse health effects (Brunekreef, Holgate 2002, Pope, Dockery 2006). A key indicator of air quality is the concentration of particulate matter with diameters smaller than 10 or 2.5 μm (PM₁₀, PM_{2.5}, respectively). 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 elemental composition of particles, but few studies have assessed the relationship between organic components and adverse health effects.

There are thousands of organic components in the particulate and gas phase of ambient air. Characterizing exposure to all individual components is not feasible so far. One approach, which has been used in many studies, is to quantify elemental (EC) and organic carbon (OC) as more generic indicators of air quality. EC is a highly polymerized dark fraction which is resistant to oxidation at temperatures below 400°C (Penner and Novak, 1996). The surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes. EC is used as an indicator for traffic diesel emissions and correlates highly with black smoke (BS), black carbon (BC) and PM absorbance (Cyrys et al. 2003, Heal, Quincey 2012, Schaap, Denier van der Gon 2007, Keuken et al. 2012). OC in contrast is a mixture of organic compounds such as aliphatic and aromatic hydrocarbons, acids, etc. Differentiation of elemental and organic carbon is usually achieved via assessment of various thermal, optical and chemical parameters.

Polycyclic aromatic hydrocarbons (PAH) are persistent organic components associated with various adverse health effects (Nielsen et al. 1996). The EU strictly limits the annual average of the PAH in ambient air. Benzo[a]pyrene (B[a]P) is used as a proxy for all PAH and is limited in ambient air to 1 ng/m³ (EUD (European Union Directive) 2005). PAH are mostly formed during incomplete combustion processes. Sources include: domestic, transportation, industrial, and agricultural processes. Domestic emissions arise from burning wood, coal, oil and garbage for heat and waste disposal. Road and maritime transportation can be significant sources of PAH although levels depend on engine type and age, and fuel used. Industrial PAH emissions originate mainly from metal and steel production, the petrochemical industry and power generation. PAH from agriculture derive mainly from open biomass burning (Ravindra et al. 2008). There are 16 PAH, known as priority PAH of United States Environmental Protection Agency (US EPA), which are often the focus of environmental studies of air quality.

Finally hopanes and steranes are components present in crude oil. They have been used as markers for motor vehicle exhaust particles in the atmosphere (Simoneit 1999). Hopanes and steranes are also present in lubricating oil used by

both gasoline- and diesel-powered motor vehicles, and are also found in diesel fuel (Cass 1998).

TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) and ESCAPE (European Study of Cohort for Air Pollution Effects) are EU FP7 funded projects designed to provide advanced knowledge on the impact of transport emissions and outdoor air pollution on human health in Europe. In selected European locations both projects combined air pollution exposure assessment to health data available from various European cohort studies (Eeftens et al. 2012).

In the framework of the ESCAPE project, 36 study areas were used to assess concentrations of NO_x and NO_2 across Europe. In 20 of those study areas $\text{PM}_{2.5}$, PM_{10} , $\text{PM}_{2.5}$ absorbance and elemental composition were additionally measured. Results of the measurements have been published (Eeftens et al. 2012b, Cyrus et al. 2012, Eeftens et al. 2012a, Beelen et al. 2013, de Hoogh et al. 2013). Within the TRANSPHORM project further $\text{PM}_{2.5}$ characterization was conducted in ten study areas. Specifically the concentrations of atmospheric EC/OC, PAH and oxidative potential were determined. Additionally, at four of these locations, hopanes/steranes and levoglucosan were analyzed. Levoglucosan and oxidative potential results will be presented elsewhere (Jedynska et al. 2015, Jedynska et al, submitted).

The aim of this work was to determine the spatial contrast of specific organic components (EC/OC, PAH and hopanes/steranes) within and between European study areas and further to assess the relationship of these components with components measured within the ESCAPE project (NO_2 , NO_x , $\text{PM}_{2.5}$ mass and absorbance). A key interest was to assess the impact of motorized traffic on PAH concentrations by investigating the relation between PAH and other markers.

Methods

Sampling campaign

The ESCAPE sampling campaign was described previously (Cyrus et al. 2012, Eeftens et al. 2012b). In ten study areas, mostly 20 sampling sites were selected (40 in the larger study areas Netherlands and Catalonia). The ten study areas selected from the 20 ESCAPE PM areas were mostly the largest cities with multiple air pollution sources and covering Europe from North to South. In the Netherlands at only 16 of the 40 ESCAPE sites the additional measurements were made because of lack of equipment (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. For extended $\text{PM}_{2.5}$ characterization two samples were collected: one on a Teflon coated glass fiber filter (T60A20, Pallflex) for analysis of organic components (PAH,

hopanes/steranes) and one on a quartz filter (QMA, Whatman) for EC/OC, oxidative potential and levoglucosan quantification. PM samples were taken with Harvard impactors, designed to collect particles smaller than 2.5 μm (PM_{2.5}) at a flow rate of 10 l/min. Identical equipment and sampling protocols were used in all study areas.

Sampling sites 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 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.

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
Finland	Helsinki/Turku	27.01.2010 – 26.01.2011	20	2	10	8
Denmark	Copenhagen	19.11.2009 – 17.11.2010	20	3	6	11
United Kingdom	London/Oxford	26.01.2010 – 18.01.2011	20	1	12	7
The Netherlands	Rotterdam, Amsterdam, Groningen, Amersfoort	17.02.2009 – 19.02.2010	16	4	4	8
Germany	Munich/Augsburg	27.10.2008 – 05.11.2009	20	5	6	9
France	Paris	04.01.2010 – 04.01.2011	20	4	9	7
Italy	Rome	27.01.2010 – 26.01.2011	20	2	8	10
Spain	Catalonia (Barcelona, Girona, Sabadell)	14.01.2009 – 14.01.2010	40	4	13	23
Greece	Athens	21.04.2010 – 27.04.2011	20	1	12	7

Adjustment for temporal variability

The three samples were used to estimate the spatial variation of the annual average level of each pollutant. Three two-weekly samples may not characterize the absolute concentration well, but the main goal of our measurements was to compare concentrations between the sites. For practical reasons, it was not possible to collect samples simultaneously at all sites at each study area. Due to temporal variation in air quality, the estimated annual average from different sampling periods at the sampling sites would result in non-comparable results. In order to correct for the temporal variation, a reference site was introduced in each study area, where the pollutants' concentrations were monitored during a full year. The reference site was chosen at regional or urban background locations, not

directly influenced by local sources. The assumption we made is that the temporal variation at the reference site reflects temporal variation in the study area. This adjustment method was used in several previous studies (Eeftens et al. 2012b, Hoek et al. 2002, Hoek et al. 2008).

Our correction procedure followed the ESCAPE procedure (Eeftens et al. 2012b, Cyrus et al. 2012). At the reference sites, the following components were measured: NO_x, NO₂, PM_{2.5}, PM₁₀ mass and absorbance. The organic components 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 measurements of specific organic components. First, the temporal correlation was calculated for each site between organic components 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 the specific organic component 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 the organic pollutant, we used the ratio method instead of the difference method, which was the default in ESCAPE. A high correlation was found between results corrected with the ratio and difference methods for PM_{2.5}, PM_{2.5} PM₁₀ and PM_{coarse} in three study areas (Stockholm County, The Netherlands/Belgium and Catalonia) (Eeftens et al. 2012b).

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

Analytical methods

EC/OC

1cm² 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 (Cavalli et al. 2009). The expanded uncertainty of the method amounted to 33%. Expanded uncertainty was calculated as 2 times the uncertainty incorporating reproducibility, recovery and accuracy of the calibration standard, following the Dutch norm NEN 7777 Environment - Performance characteristics of measurement methods.

PAH, hopanes/steranes

Analytical methods for PAH hopanes/steranes have been previously published (Kooter et al. 2011). For the current experiments the method was extended with measurements of hopanes/steranes (Wang, Stout & Fingas 2006). T60A20 filters were extracted via an accelerated solvent extraction method (ASE) with toluene. Furthermore, extracts were fractionated 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). The expanded uncertainty of the method amounted between 16 and 33%.

Levoglucosan

Analytical method for levoglucosan is described elsewhere (Jedynska et al. in preparation). Briefly, a part of each quartz filter was extracted in ethylacetate with 0.5% triethylamine. Further, extracts were derivated with silylating reagent (TMSI). Levoglucosan was measured with gas chromatography in combination with mass spectrometric detection (Agilent 6890/5973N GC/MS).

Quality control

To maximize comparability of the measurements in different countries, sampling and measurement procedures were conducted according to standard protocols. All filters were sent to project partners from one laboratory. All measurements described in this publication were performed in one laboratory – TNO in The Netherlands. Due to practical limitation, only five field blanks were taken in The Netherlands. They were used for calculation of the methods' detection limits and correct individual results. The limit of detection (LOD) was calculated as three times the standard deviation of five field blank measurements.

Data analysis

Statistical analyses were performed with the SPSS statistical program (IBM SPSS Statistics 20). Spatial variation was expressed as range (maximum – minimum) and was calculated as percentage of the mean. Student's t-tests were used to calculate the difference (and significance) between site types and seasons. To assess relationships between components the Spearman correlation was calculated.

From the 16 EPA PAH measured, eight particle-related PAH were quantified, as our sampling system did not quantitatively capture semi-volatile PAH well. Σ PAH was determined as the sum of eight particle-related PAH: benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene. We also calculated the Σ hopanes/steranes for further data analysis.

Individual measurements were used to assess seasonal differences in concentrations of the various pollutants. We performed this analysis particularly to obtain more information on the relative contribution of heating and non-heating sources. We used two definitions, one comparing samples taken in the summer (June – August) and in the winter (December – February). Because of different number of samples and in some cases relatively few samples taken in those months we decided to also analyze seasonal differences based on all individual

measurements divided into two periods: warm (April – September) and cold period (October – March).

Results

Presented results are adjusted year averages. In online supplement Table S1 the chosen components for temporal adjustment are presented with median Pearson correlation. All median temporal correlations of chosen components for adjustment were high ($0.7 < r < 0.9$) or very high ($r > 0.9$). Ratio adjusted and unadjusted year averages were mostly highly correlated (online supplement Table S2). This suggests that the adjustment did not change the results much. Moderate correlation between unadjusted and adjusted results for OC can be caused by relative large temporal variation or when measurements were performed more than once in the winter or summer.

Spatial variation within and between study areas is presented in Figure 1A-E and Table 2. Differences between site types in different study areas are presented in Table 3.

EC/OC

Atmospheric EC/OC concentrations were highest in southern European study areas and lowest in northern study areas (Figure 1A, 1B). Concentrations of OC were highest in Rome and Athens. The lowest OC concentrations were found in Helsinki. There was substantial variation within study areas. All range/mean ratios were higher than 80% (Table 2). OC concentrations at street locations were higher than at urban background locations in all study areas (Table 3). The median S/UB ratio was among the lowest of all components. The median RB/UB was 0.63, the largest contrast of all components.

The highest EC concentrations were found in southern Europe with average concentrations above $2 \mu\text{g}/\text{m}^3$. The lowest EC concentrations were measured in northern Europe. In three Scandinavian study areas, the EC average concentration was lower than $1 \mu\text{g}/\text{m}^3$. There was high variation in EC concentration within all study areas. In all study areas EC concentrations were higher at street locations than at urban background locations. The median S/UB ratio was 1.62, higher than for OC. In nine study areas average EC concentrations at RB was lower than at UB locations with a median of 0.73, a smaller difference than for OC.

PAH

PAH results showed a different trend in Europe than EC/OC. Results of all individual PAH are presented in supplement Table S3. The highest ΣPAH concentrations were found in Copenhagen and Rome with averages of 2.1 and 2.0 ng/m^3 , respectively. The lowest ΣPAH concentrations were measured in London/Oxford and Oslo with averages of 1.0 and 1.2 ng/m^3 respectively. In all

countries Σ PAH concentrations were higher at S than at UB sites., but the contrast was less than for EC. Individual PAH concentrations had similar concentration trends as Σ PAH. The highest B[a]P concentrations were found in Athens and Copenhagen, at 0.25 and 0.21 ng/m³, respectively.

Hopanes and steranes

13 hopanes and steranes were measured in four study areas: Oslo, The Netherlands, Munich/Augsburg and Catalonia (Figure 1E). Levels of individual hopanes and steranes are presented in online supplement Table S4. The highest concentrations of Σ hopanes/steranes were found in Catalonia (5.0 ng/m³)(Table 2). Catalonia with the largest number of sites were had also the highest within area variation with range/mean ratio of 297%. In all countries, S locations had higher concentrations of Σ hopanes/steranes than at UB sites. However, the median ratio was relatively small (Table 3).

Seasonal differences

Due to lack of the sampling equipment in Munich/Augsburg, no samples were taken in the winter (December – February). In other study areas the average number of samples was: 15 in the summer and 16 in the winter. All measured components had higher concentrations during winter (Figure S1 A – E, Table 4) with exception for EC in Catalonia. The highest winter/summer ratio was found for B[a]P with a median of 15.38 (4.75 – 52.15). Median winter /summer ratios of OC and Σ hopanes/steranes were similar: 2.22 and 2.54, respectively. The lowest median winter/ summer ratio was found for EC: 1.44 (0.84 – 2.56).

Seasonal differences based on all measurements showed similar trend, with higher concentrations during the cold period (Figure 2 A – E, Table 4) with exception for OC in Helsinki/Turku and Munich/Augsburg. The highest cold/warm ratio was found for B[a]P with a median of 5.04 (2.90 – 21.33), which was much lower than difference between winter and summer. Median cold/warm ratios of OC and Σ hopanes/steranes were similar: 1.88 and 1.91, respectively. The lowest median cold/warm ratio was found for EC: 1.27.

Relationships between components

Correlations between the various components differed substantially across Europe (Table 5). There was no spatial pattern in correlations across study areas. The correlation between PM_{2.5} and most components was moderate on average. In individual areas high correlations were found however. The highest correlations were found between EC and other traffic related markers, PM_{2.5}absorbance and NO_x. Correlations between EC and Σ PAH varied from low in Copenhagen to high in Oslo and Paris with median of r=0.59. Only a moderate correlation was found between EC and Σ hopanes/steranes (r = 0.59). OC correlated moderately with most of other components, the highest with PM_{2.5} (median r = 0.65). Σ PAH

correlated moderately with other components. The highest correlation was found with levoglucosan (median $r = 0.66$). Σ PAH correlated weakly with Σ hopanes/steranes ($r=0.36$). Σ hopanes/steranes correlated the highest with PM2.5 absorbance ($r=0.72$) and the lowest with levoglucosan (median $r = -0.22$).

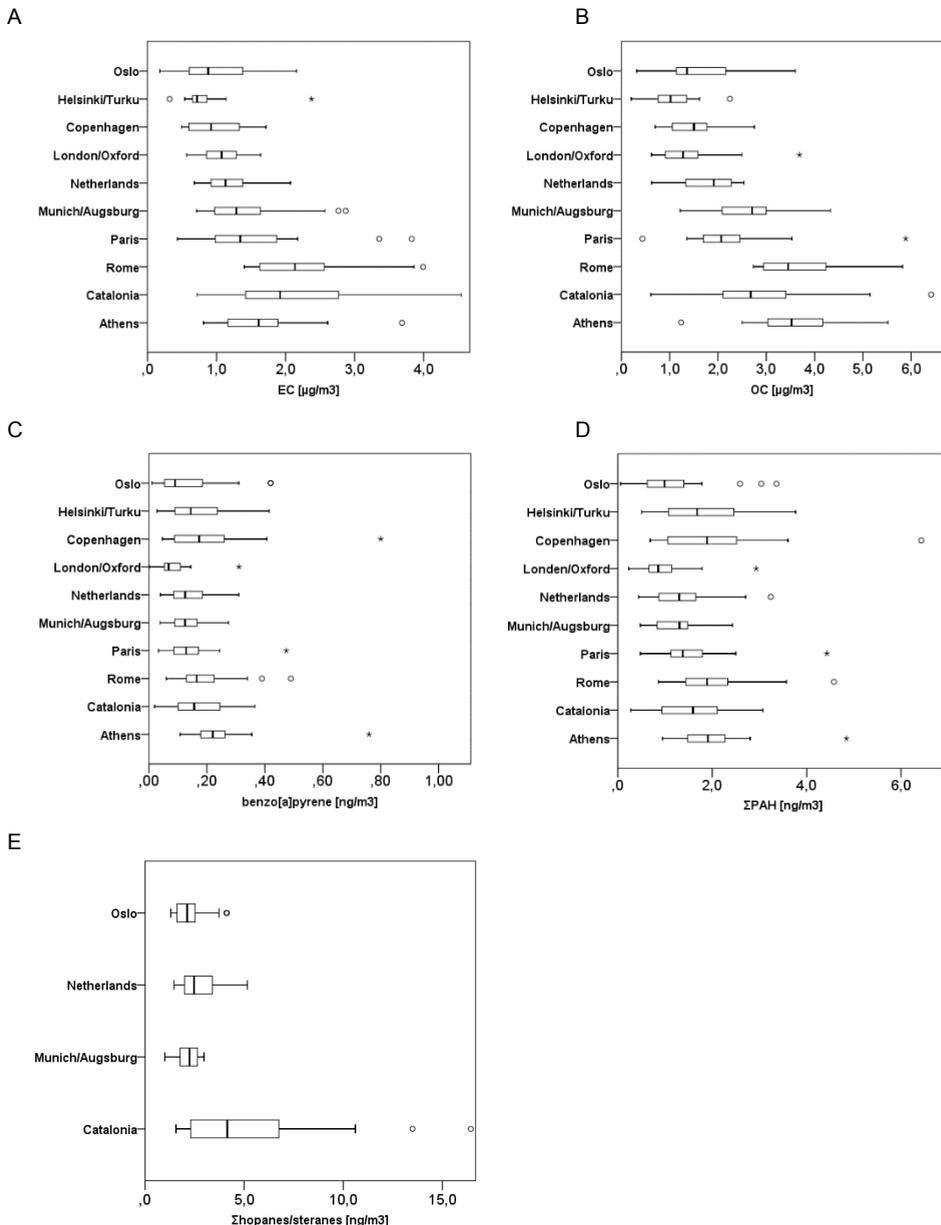


Figure 1. Distribution of the year average concentration within study areas a) OC, b) EC, c) Σ PAH, d) B[a]P e) Σ hopanes/steranes. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown.

Table 2. Mean and contrast of annual averages for 10 European study areas

Study area	n	OC			EC			ΣPAH			B[a]P			Σhopanes/steranes		
		Mean (µg/m ³)	Range	R/M (%)	Mean (µg/m ³)	Range	R/M (%)	Mean (ng/m ³)	Range	R/M (%)	Mean (ng/m ³)	Range	R/M (%)	Mean (ng/m ³)	Range	R/M (%)
Oslo	19	1.7	3.3	199	1.0	2.0	200	1.2	3.3	280	0.14	0.41	292	2.3	2.8	124
Helsinki/Turku	20	1.1	2.0	189	0.8	2.1	254	1.8	3.3	183	0.17	0.39	221	N/A	N/A	N/A
Copenhagen	20	1.5	2.1	141	1.0	1.2	124	2.1	5.7	276	0.21	0.75	352	N/A	N/A	N/A
London/Oxford	20	1.4	3.1	220	1.3	5.3	399	1.0	2.7	276	0.09	0.31	354	N/A	N/A	N/A
Netherlands	16	1.8	1.9	107	1.2	1.4	115	1.4	2.8	200	0.14	0.27	189	2.8	3.7	135
Munich/Augsburg	20	2.7	3.1	117	1.5	2.2	149	1.3	2.0	157	0.13	0.24	178	2.2	2.0	91
Paris	20	2.2	5.5	244	1.8	7.6	420	1.5	4.0	256	0.14	0.44	307	N/A	N/A	N/A
Rome	20	3.7	3.1	84	2.3	2.6	115	2.0	3.7	183	0.19	0.43	222	N/A	N/A	N/A
Catalonia	40	2.8	5.8	210	2.2	4.8	222	1.6	2.8	179	0.17	0.35	204	5.0	14.9	297
Athens	20	3.5	4.3	121	1.6	2.9	177	2.0	3.9	196	0.25	0.65	266	N/A	N/A	N/A

R/M Range/Mean
N/A not analysed

Chapter 2: Spatial variations of EC/OC, PAH and hopanes/steranes

Table 3. Ratios between different site types for individual study areas.

	OC		EC		ΣPAH		B[a]P		Σhopanes/steranes	
	Ratio		Ratio		Ratio		Ratio		Ratio	
	RB/UB	S/UB	RB/UB	S/UB	RB/UB	S/UB	RB/UB	S/UB	RB/UB	S/UB
Oslo	0.40	1.02	0.41*	2.07**	0.12	1.44	0.12	1.58	0.79	1.04
Helsinki/Turku	0.55	1.42*	0.71*	1.43	0.56	1.06	0.50	1.19	N/A	N/A
Copenhagen	0.54*	1.03	0.68	1.47**	0.91	1.07	0.85	1.10	N/A	N/A
London/Oxford	1.43	1.84**	1.15	2.17**	0.99	2.03**	1.11	2.41**	N/A	N/A
Netherlands	0.52**	1.05	0.80*	1.48**	1.06	1.88*	1.00	2.00**	1.02	1.31
Munich/Augsburg	1.34	1.32**	0.76**	1.67**	0.98	1.36	0.92	1.42	1.16	1.31*
Paris	0.70*	1.53*	0.50**	2.49**	0.60*	1.33	0.48*	1.41	N/A	N/A
Rome	1.11	1.21	0.85	1.56**	1.02	1.77**	1.12	2.08**	N/A	N/A
Catalonia	1.32	1.71**	0.75	2.03**	1.06	1.74**	1.24	2.10**	0.62	2.10**
Athens	0.38**	1.32**	0.59	1.55**	0.80	1.44*	0.68	1.55*	N/A	N/A
Median	0.63	1.32	0.73	1.62	0.94	1.44	0.89	1.56	0.90	1.31

*Significant difference between site type with $p < 0.10$

**Significant difference between site types with $p < 0.05$

N/A not analysed

Table 4. Seasonal differences expressed as concentration ratios: cold/warm (C/W), winter/summer (WIN/SUM)

Country	OC		EC		ΣPAH		B[a]P		Σhopanes/steranes	
	C/W	WIN/SUM	C/W	WIN/SUM	C/W	WIN/SUM	C/W	WIN/SUM	C/W	WIN/SUM
	Oslo	2.11**	2.41**	2.78**	2.56**	17.89**	35.39**	21.33**	45.58**	2.58**
Helsinki/Turku	0.71	1.09	1.18	1.56	3.15**	8.53**	2.90**	7.97**	N/A	N/A
Copenhagen	2.29**	3.08**	1.28**	1.43**	6.46**	31.95**	5.94**	52.15**	N/A	N/A
London/Oxford	1.83**	2.22**	1.70**	1.44**	8.00**	13.44**	10.75**	18.16**	N/A	N/A
Netherlands	1.14	2.02	1.26	1.36	3.98**	11.39**	4.55**	10.27**	2.34	2.71
Munich/Augsburg	0.84	N/A	1.27	N/A	4.04**	N/A	4.53**	N/A	1.18	N/A
Paris	1.92	2.68	0.89	1.24	3.53**	11.50**	3.75**	15.49**	N/A	N/A
Rome	2.28	1.96	1.31	1.22	4.97**	8.58**	5.52**	9.70**	N/A	N/A
Catalunya	1.74	1.61	1.20	0.84	2.80**	3.94**	3.35**	4.75**	1.47	1.91
Athens	2.00**	2.60**	1.31**	1.63**	4.88**	11.59**	6.71**	15.38**	N/A	N/A
Median	1.88	2.22	1.27	1.44	4.46	11.50	5.04	15.38	1.91	2.54

*Significant difference between site type with $p < 0.10$

**Significant difference between site types with $p < 0.05$

N/A not analysed

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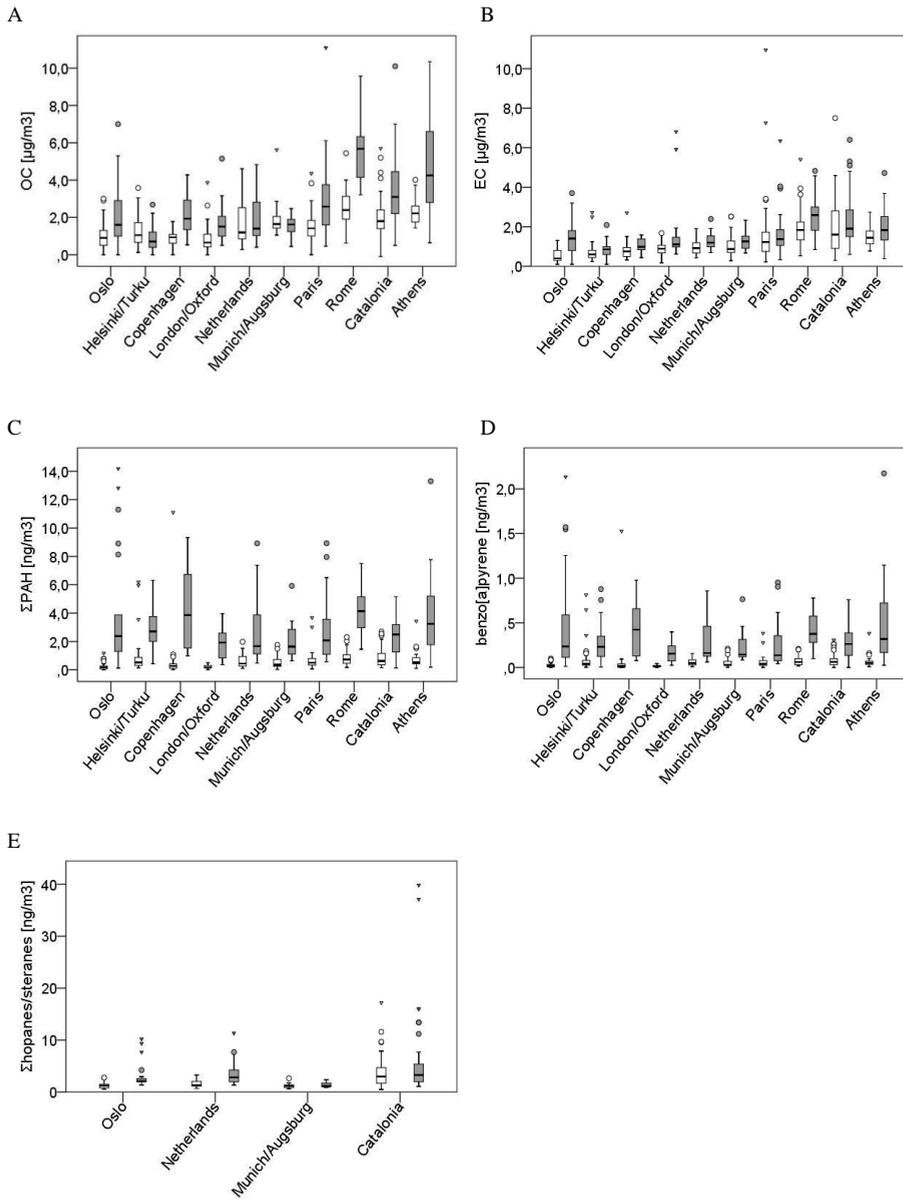


Figure 2. Seasonal differences of different components. a) OC, b) EC, c) ΣPAH , d) B[a]P, e) $\Sigma\text{hopanes/steranes}$. White box – warm period, grey box – cold period.

24 Table 5. Spearman correlations between different components

Study area	Oslo	Helsinki/ Turku	Copenhagen	London/ Oxford	Netherlands	Munich/ Augsburg	Paris	Rome	Catalonia	Athens	Median	
OC	NOx	0.40	0.49*	0.21	0.51*	0.37	0.71**	0.26	0.51**	0.83**	0.45	
	PM2.5	0.50*	0.71**	0.67**	0.49*	0.46	0.77**	0.44	0.62**	0.87**	0.65	
	PM2.5ABS	0.41	0.67**	0.34	0.65**	0.49	0.40	0.64**	0.36	0.58**	0.53	
	EC	0.49*	0.70**	0.49*	0.73**	0.48	0.27	0.66**	0.27	0.67**	0.52	
	ΣPAH	0.44	0.51*	0.60**	0.63**	0.41	-0.29	0.74**	0.28	0.61**	0.33	0.48
	B[a]P	0.43	0.54*	0.54*	0.66**	0.41	-0.35	0.68**	0.19	0.63**	0.42	0.49
	Σhopanes/steranes	0.01	N/A	N/A	N/A	0.10	0.26	N/A	N/A	0.44**	N/A	0.18
	levoglucosan	0.38	N/A	N/A	N/A	0.27	-0.36	N/A	N/A	0.22	N/A	0.24
	EC	NOx	0.95**	0.63**	0.82**	0.76**	0.95**	0.94**	0.82**	0.88**	0.70**	0.85
		PM2.5	0.81**	0.71**	0.78**	0.56*	0.82**	0.57**	0.95**	0.63**	0.77**	0.74
PM2.5ABS		0.93**	0.75**	0.86**	0.84**	0.98**	0.94**	0.96**	0.81**	0.92**	0.89	
ΣPAH		0.84**	0.54*	0.21	0.57**	0.33	0.48*	0.84**	0.65**	0.60**	0.59	
B[a]P		0.85**	0.56*	0.14	0.57**	0.51*	0.50*	0.87**	0.63**	0.59**	0.57	
Σhopanes/steranes		0.49*	N/A	N/A	N/A	0.69**	0.4	N/A	N/A	0.71**	N/A	0.59
levoglucosan		0.72**	N/A	N/A	N/A	-0.10	-0.20	N/A	N/A	-0.27	N/A	-0.15
ΣPAH		NOx	0.75**	0.07	0.03	0.58**	0.30	0.45*	0.77**	0.71**	0.59**	0.54*
		PM2.5	0.80**	0.20	0.45*	0.43	0.72**	0.02	0.84**	0.53*	0.78**	0.57
		PM2.5ABS	0.86**	0.24	0.10	0.73**	0.42	0.43	0.75**	0.75**	0.70**	0.64
	B[a]P	1.00**	0.97**	0.97**	0.97**	0.93**	0.95**	0.97**	0.99**	0.97**	0.94**	
	Σhopanes/steranes	0.55*	N/A	N/A	N/A	0.06	0.18	N/A	N/A	0.73**	N/A	0.36

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	levoglucosan	0.89**	N/A	N/A	N/A	0.74**	0.57**	N/A	N/A	0.26	N/A	0.66
B[a]P	NOx	0.77**	0.13	0.00	0.50*	0.44	0.46*	0.78**	0.69**	0.59**	0.65**	0.55
	PM2.5	0.80**	0.24	0.41	0.38	0.82**	0.00	0.85**	0.51*	0.78**	0.69**	0.60
	PM2.5ABS	0.86**	0.27	0.08	0.68**	0.57*	0.45*	0.78**	0.73**	0.70**	0.64**	0.66
	Σhopanes/ steranes	0.55*	N/A	N/A	N/A	0.12	0.17	N/A	N/A	0.71**	N/A	0.34
	levoglucosan	0.88**	N/A	N/A	N/A	0.66**	0.51*	N/A	N/A	0.32*	N/A	0.59
Σhopanes/ steranes	NOx	0.43	N/A	N/A	N/A	0.73**	0.36	N/A	N/A	0.74**	N/A	0.58
	PM2.5	0.25	N/A	N/A	N/A	0.45	0.57**	N/A	N/A	0.73**	N/A	0.51
	PM2.5ABS	0.42	N/A	N/A	N/A	0.72**	0.55*	N/A	N/A	0.79**	N/A	0.72
	levoglucosan	0.53*	N/A	N/A	N/A	-0.32	-0.42	N/A	N/A	-0.11	N/A	-0.22

Discussion

Significant contrasts were found between and within the ten study areas in terms of concentrations of organic air pollutants. EC and OC concentrations had the highest concentrations in southern and the lowest in northern Europe. PAH exhibited a different trend with similar concentrations in southern and northern European study areas. All components we examined had higher concentrations at street in comparison to background sites, with the highest contrasts for EC. The overall moderate correlation with PM_{2.5} indicates that PM_{2.5} does not fully capture the spatial variation of organic components supporting additional analysis. The seasonal analysis showed that PAH was the component that exhibited the largest increase in the cold (heating) period compared to the warm period.

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. This allowed us to obtain comparable results in ten European study areas, and assess differences between and within sites.

Contrast within and between study areas

OC and EC concentrations across Europe exhibited a similar trend as NO_x, or PM and PM absorbance reported before (Eeftens et al. 2012b, Cyrus et al. 2012). PAH concentration did not follow a north-south gradient.

It is well documented that OC can originate from multiple sources (Saarikoski et al. 2008). The higher OC concentrations in southern European study areas may be caused by higher secondary organic aerosol (SOA) formation due to more intensive oxidation of gas-phase compounds due to higher temperatures (Sillanpää et al. 2005). In terms of PAH, the European Union target average value for B[a]P is 1 ng/m³ (EUD (European Union Directive) 2005). This value was not exceeded in any of the study areas. The UK has a separate target B[a]P concentration level of 0.25ng/m³ (NAQIA 1999). Median B[a]P concentration in London/Oxford was the lowest among the study areas.

In general, our results confirm those presented in “The Air quality in Europe — 2012 report” (Guerreiro et al. 2012) where the annual average of B[a]P in Europe are presented. \sum PAH concentrations showed, for all study areas, higher variation within area than between study areas. OC had clearly the lowest variation within study area. This might be caused by the fact that OC concentrations are influenced by non-local sources: secondary organic aerosol (SOA) and long-range transport (Saarikoski et al. 2008).

Limitations of our sampling campaign include the lack of measurement of organic components at the reference site, limiting adjustment for temporal variation. We however documented that components which were measured at the reference site (NO_x and PM_{2.5} absorbance especially) were temporally highly correlated with

organic markers. at our sampling sites. This can be explained by the dominant influence of weather factors in determining temporal variation. We further collected few field blanks in the Netherlands only where the laboratory was located. The levels of field blanks taken in The Netherlands for components reported by Eeftens et al, and Cyrus et al (Eeftens et al. 2012b, Cyrus et al. 2012) had similar levels as the median blank levels for the same 10 study areas, suggesting that collection of field blanks in the central location only may not have resulted in underestimation of field blank values.

Contrasts between rural background, urban background and street sites

Concentrations of all components at all study areas were highest at street locations. However there was much variation in S/UB ratio across Europe, probably related to the composition and size of the vehicle fleet (e.g. % of diesel cars). The highest median S/UB ratio was found for EC – 1.62. For the same study areas a higher S/UB ratio was found only for NO_x – 1.8 (Cyrus et al. 2012). All organic markers had S/UB ratios higher than PM_{2.5} – 1.2 (Eeftens et al. 2012b). It was previously reported that S/UB ratio for PM_{2.5} was lower than for PM_{2.5} absorbance (Janssen et al. 2011). It can be explained by high concentrations of PM_{2.5} at the background locations caused by long-range air pollution from transport. Other pollutants have local sources e.g. EC from diesel emissions (Hamilton, Mansfield 1991), and PAH from a variety of combustion processes (Marchand et al. 2004). The PAH S/UB ratio was overall smaller than for EC, probably as a result of the larger contribution of other combustion sources than traffic (wood burning, industrial) to PAH concentrations relative to EC. Differences in dispersion are unlikely between PAH and EC, as both pollutants are primarily in submicrometer particles.

The variation of Σ PAH S/UB ratios across Europe may reflect the variation of the motorized traffic contribution relative to other PAH sources across countries. In general in southern Europe, the S/UB was higher suggesting that traffic may be a relatively more important source of PAH in southern Europe. A formal source apportionment however was not conducted.

The largest variation in differences between sites was found for OC concentrations. In some countries there was almost no difference between S and UB location (Oslo, Copenhagen, The Netherlands) while in other countries the difference was larger and more significant (London/Oxford, Catalonia). Even larger variation across Europe was found in the RB/UB ratios. In several areas RB was higher than UB (London/Oxford, Munich/Augsburg, Catalonia) and in others areas much lower (Athens, Oslo). This may be caused by presence of a specific OC source in the neighborhood of the sampling site such as combustion of biomass.

In general S/UB ratio for Σ hopanes/steranes was lower than for EC, 1.91 and 1.31 respectively for the four locations. Only in Catalonia the ratio for both components

was similar – about 2. EC is marker for diesel motor emissions while hopanes/steranes for both – diesel and gasoline vehicles (Minguillón et al. 2008). The lower S/UB for Σ hopanes/steranes than for EC might be caused by substantial contribution of diesel in comparison to gasoline emissions at street sites e.g. heavy duty vehicles. Given the complexity of the measurements, the performance in this study suggests that hopanes/steranes did not add much value to more standard traffic-related components in characterizing traffic-related air pollution contrasts.

Seasonal variations

The seasonal differences in pollutant concentrations have been presented in previous studies (Gehrig, Buchmann 2003, Menichini et al. 2007). The reasons for higher concentrations of air pollutants in winter include higher pollutant emissions (heating) and poorer dispersion because of less vertical mixing during winter. It was previously reported that particle-related PAH show larger seasonal differences than gas phase PAH (Schauer, Niessner & Poschl 2003, Prevedouros et al. 2004). However, PAH are mostly emitted during heating processes, lighter PAH are associated more with traffic emissions. In agreement with those results in our study seasonal differences were found for all pollutants. Particle-related PAH showed the largest seasonal differences of all presented pollutants, adding to the evidence that non-traffic combustion sources contribute significantly to PAH concentrations. The highest winter/summer ratio in our study was found for B[a]P in two Scandinavian study areas: Copenhagen and Oslo – 52.15 and 45.85, respectively, indicating that domestic heating is an important source of PAH. In the third Scandinavian study areas, Helsinki/Turku, much lower winter/summer ratio of B[a]P was found (7.97). This might suggest different heating technologies used for domestic heating across Scandinavian locations.

Prevedouros et al. compared seasonality of PAH in a number of locations (UK, Sweden, Finland, Arctic Canada) between 1991-2000 (Prevedouros et al. 2004). The highest cold to warm ratios of individual PAH were also found in Scandinavian countries and were also very high – above 30. Average B[a]P cold/warm ratio in London was 5.1 while in our study in London/Oxford this ratio was 18.16. We found similar winter/summer ratio in Finland for B[a]P (>7).

Viana et al. has reported seasonal differences of OC and EC in Barcelona (Viana et al. 2006). In comparison with that study we found in Catalonia slightly higher cold/warm ratio for OC, 2.22 in comparison to 1.76. EC cold/warm ratio was a bit lower in our study than this reported by Viana et al. (1.43 and 1.65, respectively).

Minguillón et al reported seasonal difference in Σ hopanes/steranes concentrations for Los Angeles. The cold/warm ratio 1.10 which is lower than the values found in our studies (average 2.54) (Minguillón et al. 2008). The difference is caused by the fact that the measurements performed in the winter took actually place between march and may with temperature 4 – 6 °C degrees lower than during summer

campaign. Another study from California, US showed much higher seasonality of hopanes/steranes, with cold/warm ratio of 5 (Ruehl, Ham & Kleeman 2011). Cold/warm ratio Σ hopanes/steranes in our study was higher than for EC, 2.54 vs. 1.43. This might be caused by the fact that hopanes/steranes behave as semi-volatile components in higher temperatures (Ruehl, Ham & Kleeman 2011).

Correlation between components

In our study, the highest spatial, rank correlation was found between EC and PM_{2.5} absorbance and NO_x (median $r = 0.89$ and $r = 0.85$, respectively). The high correlations agree with a study of Cyrus et al. who reported spatial correlations between EC, PM_{2.5} and PM_{2.5} absorbance in The Netherlands, Munich and Stockholm (Cyrus et al. 2003). In that study, the correlation between EC and PM_{2.5} absorbance was very high (>0.9). There are not many studies that have investigated spatial correlations between organic components across Europe. There was much variation between correlations between PAH and other components in our study, suggesting different sources of PAH at individual sites (traffic, wood combustion). Correlations between PAH and pollutants often used as traffic markers (EC, PM_{2.5}abs, NO_x) varied significantly across Europe. Oslo exhibited different correlation patterns in comparison to other Scandinavian countries, where Σ PAH, EC and levoglucosan correlated highly with each other. This suggests the presence of multiple sources at individual locations.

Various PAH sources were further confirmed by levels of Σ PAH correlations with levoglucosan and Σ hopanes/steranes. In Oslo, The Netherlands and Munich/Augsburg Σ PAH correlated with levoglucosan significantly and was higher than the correlation with Σ hopanes/steranes. In Catalonia Σ PAH correlated highly with Σ hopanes/steranes while with levoglucosan it did not correlate. Substantial differences in correlations between Σ hopanes/steranes and other traffic markers suggest different traffic composition in different countries. The other reason of low correlation between EC and Σ hopanes/steranes could be lower contrast of Σ hopanes/steranes concentration in comparison to EC e.g. in Oslo.

Conclusions

In conclusion, substantial variability was found in spatial patterns of EC, OC, PAH, and hopanes/steranes. EC and OC concentrations had similar trends in Europe as the previously reported components NO_x, PM and PM absorbance. The highest concentrations for those pollutants were found in southern Europe and the lowest in northern Europe. PAH exhibited a different trend in Europe. In southern and northern Europe concentrations of those pollutants were on a similar level. All components had higher concentrations at S locations in comparison to UB and RB locations. However S/UB and RB/UB ratios varied substantially between components and study areas.

Correlations between PAH and other pollutants differed substantially across Europe. This indicates that these chemical components may have other sources than motorized traffic, including wood or coal combustion. The epidemiological study on adverse health effects may help to correlate the health effects to specific components and/or their origin.

Because of the standard procedure of sampling, measurements and data analysis we were able to present comparable results of chemical PM_{2.5} composition across Europe.

The highly standardized measurement of these particle component concentrations across Europe will contribute to a consistent assessment of health effects across Europe.

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Appendix

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Table S1. List of components used for temporal correction of organic components with median Pearson temporal correlation (r)

	OC	EC	ΣPAH	B[a]P	Σhopanes/steranes
Oslo	PM2.5	PM2.5Abs	PM2.5Abs	PM2.5Abs	PM2.5Abs
r	0.900	0.996	0.982	0.975	0.956
Helsinki/Turku	PM2.5	PM2.5	NOx	NOx	
r	0.854	0.828	0.900	0.893	
Copenhagen	PM2.5	PM2.5Abs	NOx	NOx	
r	0.954	0.891	0.982	0.980	
London/Oxford	NOx	PM2.5Abs	NOx	NOx	
r	0.864	0.831	0.975	0.978	
Netherlands	PM2.5	PM2.5Abs	NOx	NOx	NOx
r	0.959	0.691	0.901	0.958	0.834
Munich/Augsburg	PM2.5	PM2.5Abs	NOx	NOx	NOx
r	0.714	0.999	1.000	1.000	0.965
Paris	NOx	PM2.5Abs	NO ₂	NO ₂	
r	0.937	0.954	0.978	0.970	
Rome	NOx	PM2.5	NOx	NOx	
r	0.938	0.791	0.987	0.977	
Catalonia	NOx	PM2.5Abs	NOx	NOx	NOx
r	0.870	0.969	0.966	0.976	0.750
Athens	PM2.5Abs	NOx	NOx	NOx	
r	0.992	0.974	0.974	0.971	

Table S2: Pearson correlation (r) between unadjusted and ratio-adjusted concentrations of OC, EC, ΣPAH, B[a]P, Σhopanes/steranes

Correlation (r) between unadjusted and ratio adjusted year average					
Study area	OC	EC	ΣPAH	B[a]P	Σhopanes/steranes
Oslo	0.87	0.96	0.97	0.97	0.82
Helsinki/Turku	0.92	0.98	0.96	0.97	
Copenhagen	0.57	0.94	0.95	0.96	
London/Oxford	0.97	1.00	0.99	0.99	
Netherlands	0.66	0.87	0.98	0.98	0.87
Munich/Augsburg	0.71	0.97	0.91	0.91	0.71
Paris	0.95	0.99	0.99	0.99	
Rome	0.87	0.98	0.90	0.93	
Catalonia	0.92	0.97	0.89	0.91	0.94
Athens	0.98	0.89	0.90	0.94	

Table S3. Individual PAH results: mean (M) (ng/m³), range (R) and range/mean (R/M) (%)

Study area	n	benzo(a)anthracene		chrysene		benzo(b)fluoranthene		benzo(k)fluoranthene		benzo(a)pyrene		indeno(1,2,3-c,d)pyrene		dibenz(a,h)anthracene		benzo(g,h,i)perylene		ΣPAH										
		M	R	R/M	M	R	R/M	M	R	R/M	M	R	R/M	M	R	R/M	M	R	M	R	R/M	M	R	R/M	M	R	R/M	
Oslo	19	0.12	0.37	308	0.20	0.58	295	0.24	0.7	294	0.14	0.50	370	0.14	0.41	292	0.14	0.38	271	0.03	0.08	245	0.18	0.45	252	1.2	3.3	279
Helsinki/ Turku	20	0.11	0.23	202	0.25	0.44	178	0.34	0.63	185	0.28	0.45	162	0.17	0.39	221	0.26	0.50	191	0.04	0.10	237	0.32	0.61	192	1.8	3.3	183
Copenhagen	20	0.17	0.61	348	0.34	0.84	246	0.43	1.03	237	0.34	1.05	312	0.21	0.75	352	0.25	0.68	272	0.04	0.14	315	0.29	0.66	231	2.1	5.7	276
London/ Oxford	20	0.08	0.26	338	0.17	0.52	300	0.20	0.36	181	0.13	0.33	253	0.09	0.31	354	0.11	0.24	212	0.02	0.05	217	0.18	0.64	366	1.0	2.7	276
Netherlands	16	0.11	0.24	215	0.25	0.57	226	0.33	0.64	194	0.18	0.41	225	0.14	0.27	189	0.18	0.32	183	0.03	0.05	174	0.20	0.31	153	1.4	2.8	200
Münich/ Augsburg	20	0.09	0.16	182	0.17	0.32	188	0.26	0.50	189	0.17	0.28	163	0.13	0.24	178	0.18	0.22	121	0.02	0.05	209	0.23	0.28	119	1.3	2.0	156
Paris	20	0.12	0.46	376	0.27	0.91	336	0.32	0.58	183	0.22	0.49	228	0.14	0.44	307	0.18	0.36	196	0.03	0.05	156	0.26	0.67	259	1.5	4.0	256
Rome	20	0.14	0.41	303	0.31	0.80	261	0.41	0.47	116	0.28	0.43	154	0.19	0.43	222	0.26	0.38	144	0.04	0.06	158	0.41	0.79	193	2.0	3.7	183
Catalonia	40	0.14	0.37	273	0.24	0.58	243	0.31	0.58	189	0.14	0.25	175	0.17	0.35	204	0.19	0.32	164	0.03	0.04	160	0.35	0.75	216	1.6	2.8	179
Athens	20	0.14	0.36	266	0.24	0.54	222	0.34	0.54	160	0.20	0.48	241	0.25	0.65	266	0.29	0.52	177	0.05	0.11	236	0.48	0.78	161	2.0	3.9	196

Table S4. Individual hopanes and steranes results

	Oslo n = 19			Netherlands n=16			Munich/Augsburg n=20			Catalonia n=40		
	Mean (ng/m3)	Range	R/M (%)	Mean (ng/m3)	Range	R/M (%)	Mean (ng/m3)	Range	R/M (%)	Mean (ng/m3)	Range	R/M (%)
Ts	0.15	0.18	119	0.16	0.20	125	0.14	0.13	94	0.26	0.59	231
Tm	0.12	0.17	143	0.14	0.20	144	0.12	0.22	175	0.23	0.80	354
H29 $\alpha\beta$	0.41	0.58	142	0.50	0.71	141	0.35	0.35	99	1.09	3.76	346
H29 $\alpha\alpha/\beta\alpha$	0.02	0.03	146	0.03	0.03	109	0.03	0.16	478	0.05	0.15	339
H30 $\alpha\beta$	0.41	0.56	136	0.51	0.71	138	0.38	0.39	102	0.94	2.75	291
H30 $\beta\alpha$	0.04	0.08	208	0.05	0.07	123	0.04	0.06	155	0.08	0.21	277
H30 $\beta\beta$	0.00	0.03	633	0.01	0.04	348	0.02	0.08	450	0.02	0.09	440
H31 S	0.35	0.44	125	0.44	0.65	147	0.34	0.39	114	0.90	2.87	320
H31 R	0.20	0.23	115	0.29	0.33	113	0.22	0.23	104	0.51	1.67	330
C27 $\alpha\beta\beta$ R	0.12	0.20	167	0.13	0.20	150	0.13	0.12	87	0.17	0.34	203
C28 $\alpha\beta\beta$ R	0.11	0.15	135	0.10	0.12	119	0.11	0.09	85	0.14	0.26	177
C27 $\alpha\alpha\alpha$ R	0.08	0.13	165	0.08	0.10	131	0.07	0.08	111	0.12	0.26	222
C29 $\alpha\beta\beta$ R	0.14	0.21	151	0.15	0.20	136	0.13	0.12	91	0.26	0.65	248
C29 $\alpha\beta\beta$ S	0.13	0.18	138	0.15	0.24	163	0.12	0.14	116	0.25	0.66	260
Σ HopanesSteranes	2.29	2.83	124	2.75	3.70	135	2.18	1.98	91	5.00	14.9	298

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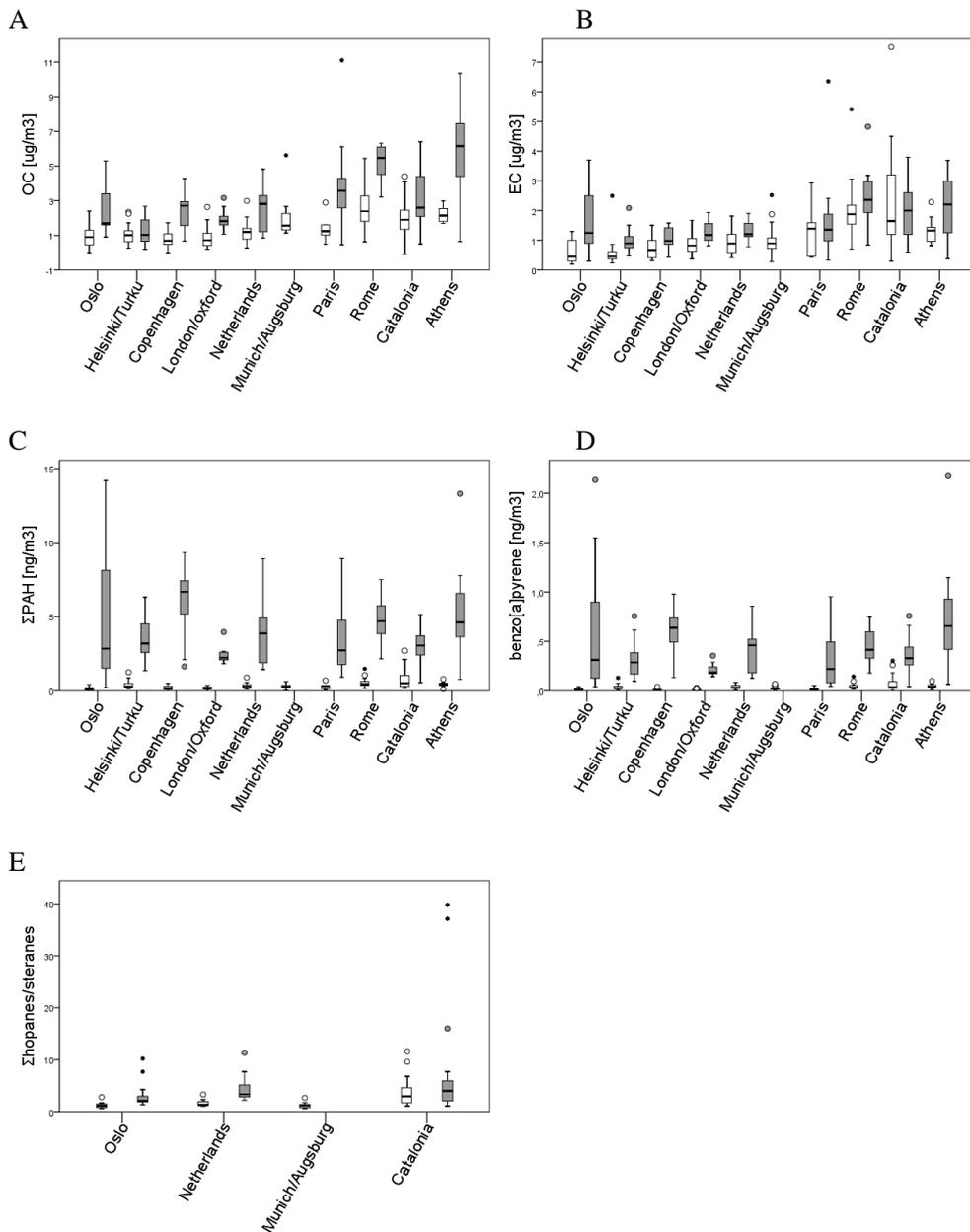


Figure S1. Seasonal differences of different components. a) OC, b) EC, c) ΣPAH, d) B[a]P, e) Σhopanes/steranes. White box – summer, grey box – winter.

Development of land use regression models for elemental, organic carbon, PAH, and hopanes/steranes in 10 ESCAPE/TRANSPHORM European study areas

Aleksandra Jedynska
Marloes Eeftens
Christophe Ampe
Francesco Forastiere
Audrey De Nazelle
Kirsten T. Eriksen
Kees Meliefste
Ole Raaschou-Nielsen

Gerard Hoek
Josef Cyrus
Rob Beelen
Marta Cirach
Wenche Nystad
Konstantina Dimakopoulou
Mark J. Nieuwenhuijsen
Bert Brunekreef

Meng Wang
Menno Keuken
Giulia Cesaroni
Kees de Hoogh
Christophe Declercq
Timo Lanki
Tarja Yli-Tuomi
Ingeborg M. Kooter

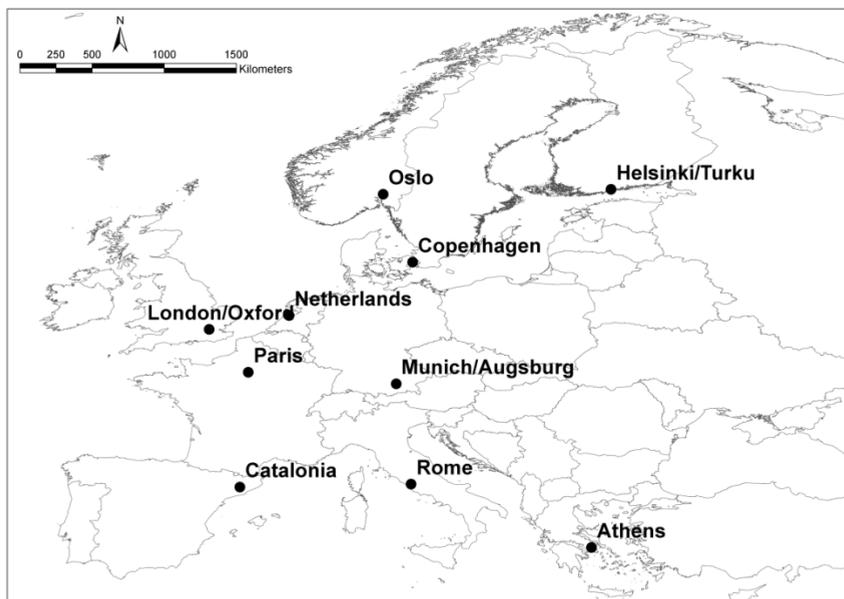
Abstract

Land use regression (LUR) models have been used to model concentrations of mainly traffic related air pollutants (nitrogen oxides (NO_x), particulate matter (PM) mass or absorbance). Few LUR models are published of PM composition, whereas the interest in health effects related to particle composition is increasing.

The aim of our study was to evaluate LUR models of polycyclic aromatic hydrocarbons (PAH), hopanes/steranes and elemental and organic carbon (EC/OC) content of PM_{2.5}.

In 10 European study areas PAH, hopanes/steranes and EC/OC concentrations were measured at 16–40 sites per study area. LUR models for each study area were developed based on annual average concentrations and predictor variables including traffic, population, industry, natural land obtained from geographic information systems.

The highest median model explained variance (R^2) was found for EC – 84%. The median R^2 was 51% for OC, 67% for benzo[a]pyrene and 38% for sum of hopanes/steranes, with large variability between study areas. Traffic predictors were included in most models. Population and natural land were included frequently as additional predictors. The moderate to high explained variance of LUR models and the overall moderate correlation with PM_{2.5} model predictions support the application of especially the OC and PAH models in epidemiological studies.



Introduction

Many studies have documented adverse health effects of exposure to ambient air pollution (Brunekreef, Holgate 2002, Pope, Dockery 2006, WHO2013). Particulate matter (PM) with diameters smaller than 10 or 2.5 μm (PM₁₀, 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, Fussell 2012). Epidemiological studies have started to assess chemical composition of particles, but few studies have assessed the relationship between specific organic components and long-term adverse health effects. In the recently published studies from the US National Particle Components Toxicity (NPACT) Initiative on health effects of particle composition, the focus was on elemental composition supplemented with elemental and organic carbon measurements (Vedal et al. 2013, Lippmann et al. 2013). Limited availability of measurements with a sufficient spatial resolution and models of organic components of particles have contributed to the small number of studies that have assessed health effects of organic PM components.

One approach, which has been used in air quality studies, is to quantify elemental (EC) and organic carbon (OC) as more generic indicators of air quality. EC is a highly polymerized dark fraction which is resistant to oxidation at temperatures below 400°C (Penner, Novakov 1996). EC is used as an indicator for traffic diesel emissions and correlates highly with black smoke (BS), black carbon (BC) and PM absorbance (Cyrus et al. 2003, Heal, Quincey 2012, Schaap, Denier van der Gon 2007, Keuken et al. 2012). EC has been linked in epidemiological studies with short and long-term health effects (Janssen et al. 2011). OC in contrast is a mixture of organic compounds such as aliphatic and aromatic hydrocarbons and acids. OC has been included in epidemiological studies less often than elemental carbon. There is evidence of OC associations with short-term adverse health effects (Kim et al. 2012, Kim et al. 2012, Kim et al. 2012, Kim et al. 2012, Kim et al. 2012, Son et al. 2012). Recently long-term exposure to OC was associated with heart disease and pulmonary mortality (Ostro et al. 2011) and cardiovascular mortality (Vedal et al. 2013).

Polycyclic aromatic hydrocarbons (PAH) are persistent organic components formed during incomplete combustion processes. Sources include: domestic, transportation, industrial, and agricultural processes. Domestic emissions arise from burning wood, coal, oil and garbage for heat and waste disposal. Road and maritime transportation can be significant sources of PAH depending on engine type and age, and fuel used. Industrial PAH emissions originate mainly from metal and steel production, the petrochemical industry and power generation. PAH from agriculture derive mainly from open biomass burning (Ravindra, Sokhi & Van

Grieken 2008). PAH has been associated with various adverse health effects (Nielsen et al. 1996, Delfino et al. 2010) but has not been evaluated in the major cohort studies on long-term air pollution exposure and mortality / lung cancer. The EU limits the annual average concentration of benzo[a]pyrene (B[a]P) as a proxy for all PAH in ambient air to 1 ng/m^3 (EUD (European Union Directive) 2005)

Hopanes and steranes are components present in crude oil. They have been used as markers for motor vehicle exhaust particles in the atmosphere. Hopanes and steranes are also present in lubricating oil used by both gasoline- and diesel-powered motor vehicles, and are also found in diesel fuel (Cass 1998). Hopanes and steranes have been associated with lung toxicity (McDonald et al. 2004), but have not been used as exposure metrics in epidemiological studies.

Land use regression models are used to describe spatial variation of the annual concentration of a pollutant, often as a tool for exposure assessment in epidemiological studies (Hoek et al. 2008). Most modeled pollutants are PM_{2.5}, PM₁₀ and compounds strongly affected by traffic (NO_x, PM absorbance, EC) (Beelen et al. 2013, Eeftens et al. 2012a). Few LUR models have been developed for pollutants for which traffic is not a major source. Recently, LUR models were developed for the elemental composition of PM_{2.5} and PM₁₀ in 20 European study areas (de Hoogh et al. 2013, de Hoogh et al. 2013). Three North American studies presented LUR models for wood smoke (Larson et al. 2007, Su et al. 2008, Smargiassi et al. 2012). Within the framework of NPACT, LUR models for EC and OC were developed. LUR models for PAH concentrations were developed in an American study (Noth et al. 2011).

Within the framework of two European projects: ESCAPE (European Study of Cohorts for Air Pollution Effects) and TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) concentrations of NO_x, NO₂, PM_{2.5}, PM₁₀, PM_{2.5} absorbance and elemental composition of PM_{2.5} and PM₁₀ were measured in 20 European study areas. The spatial variation and LUR models for these pollutants have been published (Beelen et al. 2013, Eeftens et al. 2012a, Eeftens et al. 2012b, de Hoogh et al. 2013). The ESCAPE LUR models have been used to assess exposure for epidemiological studies (Beelen et al. 2014). Additionally specific organic components (EC/OC, PAH and hopanes/steranes) were measured in 10 of the areas. The spatial variation of concentrations within and between the ten European study areas was published (Jedynska et al. 2014).

The aim of this paper is the development and evaluation of LUR models for EC, OC, PAH and hopanes/steranes. A second aim was to assess the correlation of the predictions of the new models with the already published model predictions for PM_{2.5} and NO_x.

Methods

Sampling campaign and analyses

The ESCAPE sampling campaign including the organic component characterization was described previously (Cyrus et al. 2012, Eeftens et al. 2012b, Jedynska et al. 2014). Briefly, the monitoring campaign was conducted in 10 study areas across Europe between October 2008 and April 2011 (Table 1, online supplement figure S1) and common standardized procedures were used across the study areas. Maps of the study areas can be found in the supporting information of Eeftens et al. (Eeftens et al. 2012b). 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. Monitoring was performed using the Harvard impactor, which collects PM_{2.5} and PM₁₀ on separate Teflon filters using an air flow of approximately 10 L/min. For extended PM_{2.5} characterization two additional samples were collected: one on a Teflon coated glass fiber filter (T60A20, Pallflex) for analysis of 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. In most study areas, PM concentrations were measured at 20 monitoring sites. In Catalonia 40 sites were measured and in The Netherlands organic components were measured at 16 of the 40 ESCAPE sites because of lack of additional sampling equipment. In each study area, NO_x only measurements were conducted at 20 locations (40 in Catalonia and the Netherlands). Sampling sites were divided into three groups according to traffic intensity: street sites (S), urban background (UB) and regional background (RB), using common criteria. One reference site, located in an urban or rural background location depending on the study area, was established to measure continuously for 2-week periods during a full year to adjust for temporal variation. This site was used in the calculation of the temporally adjusted annual average concentrations. Annual averages were calculated after adjusting for temporal variation measured at the continuous reference site. For each of the three sampling periods, the ratio of the concentration measured in that period from the overall annual mean at the reference site was used as adjustment, following previously published procedures (Jedynska et al. 2014).

Table 1. Description of study areas

Country	Study area	Sampling period	Sites	Site types		
				RB	UB	S
Norway	Oslo	05.02.2009 – 29.01.2010	19	2	9	8
Finland	Helsinki/Turku	27.01.2010 – 26.01.2011	20	2	10	8
Denmark	Copenhagen	19.11.2009 – 17.11.2010	20	3	6	11
United Kingdom	London/Oxford	26.01.2010 – 18.01.2011	20	1	12	7
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
France	Paris	04.01.2010 – 04.01.2011	20	4	9	7
Italy	Rome	27.01.2010 – 26.01.2011	20	2	8	10
Spain	Catalonia (Barcelona, Girona, Sabadell)	14.01.2009 – 14.01.2010	40	4	13	23
Greece	Athens	21.04.2010 – 27.04.2011	20	1	12	7

Analytical methods

Analytical methods were previously described (Jedynska et al. 2014). Briefly, quartz filters were 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 (Cavalli et al. 2009). T60A20 filters were extracted via an accelerated solvent extraction method (ASE) with toluene. Extracts were fractionated into three fractions via a silica column. This separated hopanes/steranes from PAH and PAH derivatives. 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). From the 16 EPA PAH measured, eight particle-related PAH were quantified, as our sampling system did not quantitatively capture semi-volatile PAH well. Σ PAH was determined as the sum of eight particle-related PAH: benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene. For budgetary reasons, hopanes/steranes were only measured in four study areas.

GIS predictor data

The description of available geographical information system (GIS) predictor variables has been presented in detail (Beelen et al. 2013, Eeftens et al. 2012a). The predictor variables chosen for LUR development describe potential emission sources like traffic, industry or population density. The values of predictor variables were determined for each sampling site using GIS. Geographic data were obtained

from two sources: central and local. Central data sets included: information on roads with a road classification (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). If available, local GIS data were collected on road network with linked traffic intensities, land use, population density and altitude. Each variable was calculated in several circular buffers from the sampling site (e.g. 25, 50, 100). Traffic variable buffers started at 25m because significant variation has been found at small distances from roads. Land use variable buffers started at 100 meter as these variables may represent variability in urban background concentrations. Variables with at least 5 non-zero values were used in model development. A detailed description of predictor variables including the buffer sizes and the a priori specified direction of effect on the pollutant concentration are presented in online supplement table S1.

LUR model development

LUR models for all study areas were developed centrally at IRAS. We followed the method used in the ESCAPE study Briefly, adjusted annual average concentrations of pollutants and predictor variables were used for LUR development. A supervised stepwise method was used to obtain the linear regression model with the highest adjusted explained variance (R^2). First, all predictor variables were offered separately and the variable with the highest R^2 having a slope in the a priori specified direction was selected. Next variables were added to the model one by one based on the highest adjusted R^2 if it improved model's adjusted R^2 with at least 1% and had the same effect direction as decided a priori.

The following diagnostics were used for the final model check: significance of individual variables (p -value < 0.1), collinearity test (variance inflation factor (VIF) lower than 3) and influential observation test (Cook's D value lower than 1) and Morans'I – spatial autocorrelation of the model residuals. If an influential observation determined by a too high Cook's D value was caused by extreme measured concentrations, we additionally developed LUR models without the observation. An outlier was defined as a concentration higher than the 75th percentile plus four times the interquartile range: $c_o > P75 + 4*(P75-P25)$, where $P75 - 75^{\text{th}}$ percentile, $P25 - 25^{\text{th}}$ percentile.

The performance of the final model was evaluated with leave-one-out cross validation (LOOCV). Each site was sequentially left out from the model while the included variables were left unchanged. Predicted pollutant concentration were compared with measured concentration at the excluded site. This procedure was repeated for all sites included in the model development.

We developed LUR models for EC, OC, Σ PAH, B[a]P, chrysene and Σ hopanes/steranes. As individual PAHs correlated with each other very highly in all

study areas we developed LUR models for only two individual PAHs: B[a]P and chrysene in addition to Σ PAH.

B[a]P is used in air quality guidelines as a surrogate for all PAH (EUD (European Union Directive) 2005). Chrysene was chosen because of its relatively high concentrations in comparison with other PAH, its higher correlation with traffic markers (Table S2) (Jedynska et al. 2014).

To further assess the added value of the organic components to characterize the air pollution mixture, the correlation of LUR model predictions with predictions of the already published LUR models for fine particles was calculated. We selected PM_{2.5} and PM_{2.5} absorbance. The correlation was calculated at the (20 – 40) NO₂ measurement sites in each area which were not used for model development but did have GIS predictor variables.

Results

Measured concentrations of pollutants

Substantial variability was found in measured concentrations of EC, OC, Σ PAH, B[a]P, chrysene and Σ hopanes/steranes within and between study areas (Figure 1, Table S3). The highest concentrations of EC and OC were found in southern Europe and the lowest in northern Europe. PAH concentrations exhibited a different trend in Europe, with similar concentrations in southern and northern Europe. For all components higher concentrations were measured at street locations in comparison to urban background and regional background locations (Jedynska et al. 2014).

Land use regression modelling

The final models of EC, OC, Σ PAH, B[a]P, chrysene and Σ hopanes/steranes are presented in Tables 2 to 4 and Supplementary information tables S4, S5 and S6. Figures S2 to S7 show predicted versus measured concentrations.

EC models

In all 10 study areas LUR models could be developed (Table 2). Explained variance was high in all areas, ranging from 73% for Catalonia to 95% in Oslo and the Netherlands (median 87%). The median LOOCV R² was 80%. Differences between R² and LOOCV R² was lower than 11% in all study areas indicating that models were stable. In all models traffic related variables were used, mostly describing local traffic (nearest road or buffer \leq 100m). In 8 of the 10 models, traffic intensity was included, sometimes in combination with road length variables. The Rome model contained only traffic variables, but all other models included non-traffic predictors such as population or address density often in large buffers (1000 or 5000m). In Helsinki, Rome and Paris single street sites were very influential

because of very high EC concentrations which were identified as outliers (Figure 1). Models are presented without the outliers.

OC models

In all study areas LUR models for OC could be developed (Table 3). In general explained variance of OC LUR models was lower than for EC models. The explained variance varied from 27% in Rome to 81% in London/Oxford (median 59%). The difference between model R^2 and LOOCV R^2 was larger than for EC indicating less stable models. In 8 models traffic variables were used, of which 2 models contained only traffic predictors (Rome, London). Most models contained non-traffic predictors particularly natural land and population / address density variables, often in smaller buffers than for EC. In Copenhagen and Helsinki/Turku, models with a single non-traffic predictor were identified.

B[a]P models

In two locations -Copenhagen and Helsinki/Turku- LUR models could not be developed due to influential sites which were not identified as outliers (Table 4). The median model R^2 was 67%, with a range from 31% (Munich/Augsburg) to 87% (London/Oxford). In all 8 developed models traffic variables were used. Three models included only traffic predictors (Munich, Rome and Athens). In five models, population or natural land use were additionally included.

Σ PAH models

In general, Σ PAH model performance and structure was very similar to B[a]P models (Supplemental Information Table S4). Because of the same sites as in the case of B[a]P models it was not possible to develop models in Helsinki/Turku and Copenhagen. For the eight Σ PAH models a moderate median R^2 of 65% was found.

Chrysene models

Chrysene models were slightly better than B[a]P models (Table S5). Fewer areas had low cross-validation R^2 compared to B[a]P. Models could be developed for 9 study areas. Only for Copenhagen it was not possible to build a LUR model due to an influential site. The median explained variance of the chrysene models was 71%. In Helsinki/Turku and Athens models with only one variable were developed with the low R^2 . In eight models, traffic variables were included. Only in Paris three non-traffic variables were used. The better performance compared to B[a]P is likely due to the larger impact of traffic on chrysene.

Σ hopanes/steranes models

Σ hopanes/steranes models were developed in all four study areas with measurements available (Supplemental Information Table S6). The models had the

lowest explained variance of all modeled components (median $R^2 = 43\%$). In Oslo and Catalonia, models with low R^2 ($<30\%$) were developed including one non-traffic variable. In The Netherlands, the model with the highest R^2 was developed – 78%. The model included one traffic variable, population and they coordinate indicating lower concentrations in the north. The Munich/Augsburg model included two traffic variables and a coordinate indicating higher concentrations in the east.

Additional analyses

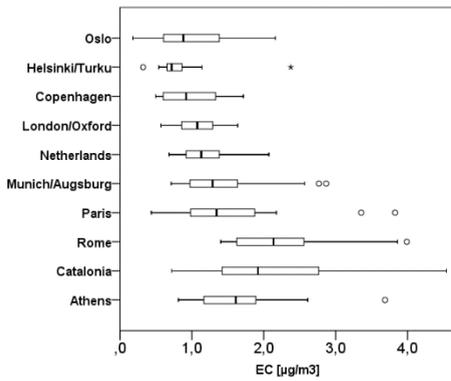
Most models explained more variation for street than for urban background locations (figures S2 –S7). The average model R^2 was 19% higher at street sites. Averaged over the five pollutants measured in 10 areas, the models with the lowest R^2 were found in Helsinki and Copenhagen and the models with the highest R^2 in London and Paris (Table S7).

Comparison of LUR PM component model predictions and LUR predictions from PM2.5, PM2.5 absorbance models

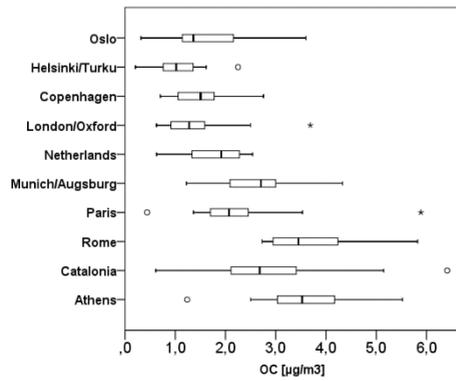
Correlations between predictions of the newly developed LUR PM component models with already published model predictions for PM2.5, PM2.5 and absorbance at monitoring sites not used in model development are shown in Table 5. Correlations varied with study area and component, e.g. in London most correlations were high and in Munich correlations with PM2.5 model predictions were very low. Moderate to high correlations were found between the EC and PAH models and PM2.5 absorbance. OC correlated less with PM2.5 absorbance, but showed a moderately high correlation with PM2.5.

Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

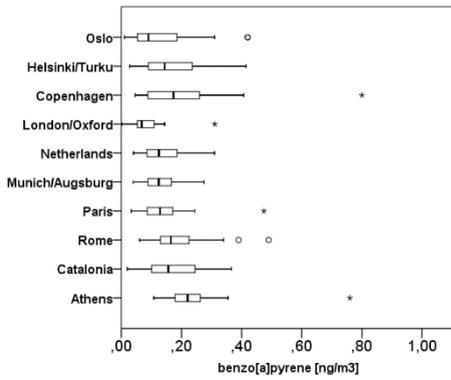
A



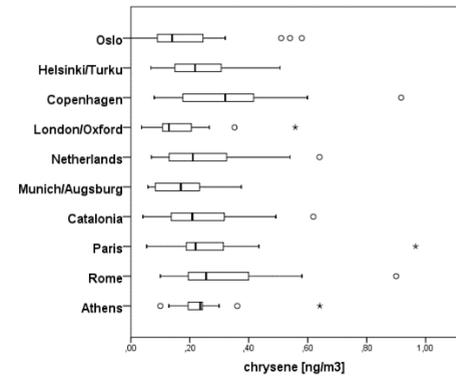
B



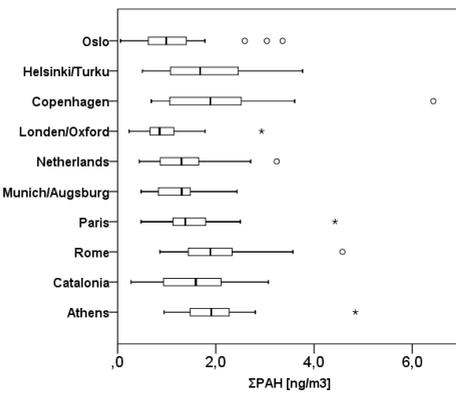
C



D



E



F

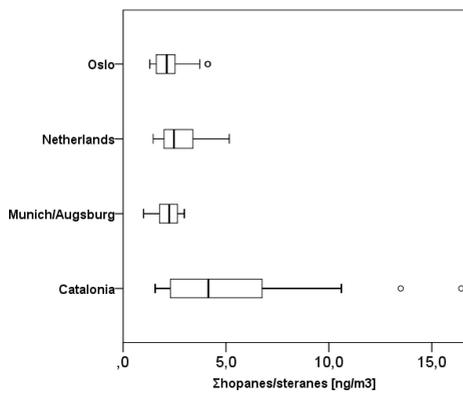


Figure 1. Distribution of the annual average measured concentrations within study areas a) EC, b) OC c) B[a]P, d) chrysene, e) ΣPAH, f) Σhopanes/steranes

52 Table 2. Description of land use regression models for EC ($\mu\text{g}/\text{m}^3$)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE ($\mu\text{g}/\text{m}^3$)	Measured concentration ($\mu\text{g}/\text{m}^3$)
Oslo	$0.915 + 3.444 \times 10^{-12} \times \text{TRAFLOAD}_{1000} + 8.185 \times \text{DISTINVMajor1} - 0.0342 \times \text{SQRALT}$	19	95	92	0.141	0.99 [0.18 - 2.16]
Helsinki/Turku	$0.738 - 2.583 \times 10^{-7} \times \text{URBNATURAL}_{1000} + 0.000293 \times \text{ROADLENGTH}_{100} + 0.000595 \times \text{ROADLENGTH}_{50}$	19	79	68	0.087	0.81 [0.32 - 2.38]
Copenhagen	$0.526 + 0.0002764 \times \text{MAJORROADLENGTH}_{300} + 3.622 \times 10^{-8} \times \text{TRAFMAJORLOAD}_{100} - 1.805 \times 10^{-7} \times \text{URBNATURAL}_{1000}$	20	87	78	0.146	0.98 [0.49 - 1.72]
London/Oxford	$0.692 + 0.000237 \times \text{INTMAJORINVDIST} + 0.000143 \times \text{HEAVYTRAFMAJOR} + 43.793 \times \text{DISTINVMajor2} + 1.111 \times 10^{-8} \times \text{HDRES}_{5000}$	19	85	77	0.131	1.32 [0.57 - 5.84]
Netherlands	$0.583 + 0.00116 \times \text{ROADLENGTH}_{50} + 3.114 \times \text{DISTINVMajor1} + 9.992 \times 10^{-7} \times \text{POP}_{5000}$	16	95	90	0.103	1.21 [0.68 - 2.07]
Munich/Augsburg	$0.821 + 0.00572 \times \text{MAJORROADLENGTH}_{50} + 0.0000139 \times \text{TRAFNEAR} + 7.699 \times 10^{-7} \times \text{POP}_{5000}$	20	86	81	0.265	1.45 [0.71 - 2.87]
Paris	$0.689 + 3.968 \times 10^{-7} \times \text{TRAFLOAD}_{50} + 9.750 \times 10^{-6} \times \text{POP}_{1000} + 3.422 \times 10^{-8} \times \text{INDUSTRY}_{5000}$	19	95	91	0.215	1.82 [0.44 - 8.08]
Rome	$1.582 + 3.313 \times 10^{-7} \times \text{TRAFMAJORLOAD}_{50} + 0.000330 \times \text{MAJORROADLENGTH}_{300}$	20	75	65	0.430	2.26 [1.40 - 3.99]
Catalonia	$1.579 + 0.000521 \times \text{INTMAJORINVDISTI} - 2.343 \times 10^{-8} \times \text{NATURAL}_{5000} + 2.536 \times 10^{-7} \times \text{HDRES}_{1000}$	40	73	66	0.604	2.15 [0.72 - 5.50]
Athens	$0.125 + 9.366 \times 10^{-7} \times \text{TRAFLOAD}_{25} + 2.820 \times 10^{-7} \times \text{PORT}_{5000} + 0.0108 \times \text{DISTINVNEARC2} + 0.00001837 \times \text{TRAFMAJOR} + 1.683 \times 10^{-8} \times \text{HDRES}_{5000}$	20	93	91	0.207	1.62 [0.81 - 3.69]
Median			87	80		

Variables used in the models: DISTINVMajor1 Inverse distance to the nearest major road (local road network), major road – road with intensity > 5,000 m/h^2 , DISTINVMajor2 Inverse distance to the nearest major road squared (local road network), DISTINVMajorC1 Inverse distance to the nearest major road (central road network), DISTINVMajorC2 Inverse distance to the nearest major road squared (central road network), INTMAJORINVDIST1 Product of traffic intensity on nearest major road and inverse of distance to the nearest major road, DISTINVNEARC2 Distance to the nearest major road squared (central road network), INTINVDIST Product of traffic intensity on nearest road and inverse of distance to the nearest road, HEAVYINTINVDIST2 Product of Heavy-duty traffic intensity on nearest road and inverse of squared distance to the nearest road, heavy duty traffic – trucks, TRAFLOAD Total traffic load of all roads in a buffer (sum of (traffic intensity * length of all segments), TRAFNEAR Traffic intensity on nearest road, TRAFMAJOR Traffic intensity on nearest major road, ROADLENGTH Road length of all roads in a buffer, MAJORROADLENGTH Road length of major roads in a buffer, TRAFMAJORLOAD Total traffic load of major roads in a buffer (sum of (traffic intensity * length of all segments), HEAVYTRAFMAJOR Heavy-duty traffic intensity on nearest major road, URBANATURAL Urban green area, NATURAL Semi-natural and forested areas, UGNI Combined urban green and natural land, PORT Port, HDRES High density residential land, LDRES Low density residential land, POP Number of inhabitants, INDUSTRY Industry area, SQRALT Squared altitude, BUILDINGS_I Area of buildings, YCOORD, XCOORD, XPLUSY Coordinate variables

Table 3. Description of land use regression models for OC ($\mu\text{g}/\text{m}^3$)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE ($\mu\text{g}/\text{m}^3$)	Measured concentration ($\mu\text{g}/\text{m}^3$)
Oslo	$0.732 - 0.00000573 \times \text{NATURAL_300} + 0.00683 \times \text{ROADLENGTH_50} + 2.429 \times \text{INTMAJORINVDIST}$	19	59	34	0.621	1.65 [0.32 - 3.60]
Helsinki/Turku	$1.393 - 0.00000580 \times \text{URBNATURAL_300L}$	20	42	32	0.362	1.08 [0.21 - 2.25]
Copenhagen	$0.410 + 0.00000488 \times \text{BUILDINGS_L_300}$	20	35	25	0.441	1.45 [0.70 - 2.75]
London/Oxford	$0.886 + 109.599 \times \text{DISTINVMAJORC2} + 0.000181 \times \text{HEAVYTRAFAJAJOR}$	20	81	74	0.326	1.39 [0.63 - 3.69]
Netherlands	$0.480 + 4.798 \times 10^{-7} \times \text{LDRES_1000} + 0.00397 \times \text{ROADLENGTH_25}$	16	80	71	0.279	1.78 [0.63 - 2.54]
Munich/Augsburg	$-112.391 - 0.406 \times \text{SQRALT} + 0.000224 \times \text{INTINVDIST} + 0.0000126 \times \text{XPLUSY}$	20	59	39	0.506	2.66 [1.22 - 4.33]
Paris	$0.894 + 0.000314 \times \text{MAJORROADLENGTH_500} + 0.0000278 \times \text{LDRES_100}$	20	79	69	0.528	2.23 [0.44 - 5.89]
Rome	$3.396 + 3.3128 \times 10^{-7} \times \text{TRAFLOAD_50}$	20	27	10	0.778	3.70 [2.73 - 5.82]
Catalonia	$2.602 + 0.00360 \times \text{INTMAJORINVDIST2} - 8.237 \times 10^{-7} \times \text{NATURAL_1000}$	40	44	30	0.895	2.76 [0.62 - 6.41]
Athens	$0.812 + 0.00177 \times \text{MAJORROADLENGTH_100} + 0.000896 \times \text{ROADLENGTH_100} + 5.199 \times 10^{-9} \times \text{TRAFLOAD_500}$	20	77	68	0.472	3.53 [1.24 - 5.52]
Median		59		37		

54 Table 4. Description of land use regression models for B[a]P (ng/m³)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE (ng/m ³)	Measured concentration (ng/m ³)
Oslo	$0.158 + 9.402 \times 10^{13} \times \text{TRAFLOAD_1000} - 0.00848 \times \text{SQRALT}$	19	70	57	0.0713	0.14 [0.01 - 0.42]
Helsinki/Turku*	-	20				0.78 [0.03 - 0.42]
Copenhagen*	-	20				0.21 [0.05 - 0.80]
London/Oxford	$0.0666 + 0.0000350 \times \text{INTMAJORINVDIST} - 2.165 \times 10^{-9} \times \text{URBGREEN_5000} + 0.0000131 \times \text{MAJORROADLENGTH_500}$	20	87	78	0.0251	0.09 [0.00 - 0.31]
Netherlands	$0.143 + 0.000695 \times \text{MAJORROADLENGTH_50} - 4.151 \times 10^{-9} \times \text{UGNL_5000}$	16	64	39	0.0489	0.14 [0.04 - 0.31]
Munich/Augsburg**	$0.108 + 0.000255 \times \text{MAJORROADLENGTH_100}$	20	31	14	0.0501	0.13 [0.04 - 0.28]
Paris**	$0.0108 + 0.0000250 \times \text{MAJORROADLENGTH_500} + 0.00000144 \times \text{LDRES_100} - 7.793 \times 10^{-9} \times \text{URBGREEN_5000} + 3.208 \times 10^{-9} \times \text{LDRES_5000}$	20	87	66	0.0400	0.14 [0.03 - 0.47]
Rome	$0.111 + 2.169 \times \text{DISTINVMajor1} + 0.000174 \times \text{MAJORROADLENGTH_100}$	20	77	69	0.0548	0.19 [0.06 - 0.49]
Catalonia	$0.0752 + 0.0000311 \times \text{INTMAJORINVDISTI} + 1.115 \times 10^{-7} \times \text{HDRES_500}$	40	39	29	0.0732	0.17 [0.02 - 0.37]
Athens	$0.176 + 1.363 \times 10^{-8} \times \text{TRAFMAJORLOAD_25} + 7.517 \times 10^{-11} \times \text{TRAFMAJORLOAD_500}$	19	38	18	0.0574	0.25 [0.11 - 0.76]
Median			67	48		

* no model possible due to an influential site

** too high Cook's D value

Table. 5 Correlations (R^2) between predicted values of PM component and LUR PM2.5 and PM2.5 absorbance at the NO_x only sites not used for model development in each study area

Study area	Component	EC	OC	ΣPAH	B[a]P	Chrysene	Σhopanes/steranes
Oslo	PM2.5	0.60**	0.36**	0.54**	0.55**	0.47**	0.34**
	PM2.5abs	0.31*	0.06	0.30*	0.30*	0.14	0.28*
Helsinki/Turku	PM2.5	0.18	0.07	NM	NM	0.27*	NA
	PM2.5abs	0.24*	0.25*	NM	NM	0.47**	NA
Copenhagen	PM2.5	0.49**	0.67**	NM	NM	NM	NA
	PM2.5abs	0.83**	0.26*	NM	NM	NM	NA
London/Oxford	PM2.5	0.85**	0.60**	0.66**	0.84**	0.64**	NA
	PM25abs	0.73**	0.86**	0.84**	0.68**	0.81**	NA
Netherlands	PM2.5	0.18*	0.02	0.21**	0.35**	0.26**	0.11
	PM2.5abs	0.42**	0.06	0.11*	0.23**	0.15*	0.18*
Munich/Augsburg	PM2.5	0.00	0.07	0.00	0.00	0.03	0.39**
	PM2.5abs	0.54**	0.00	0.59**	0.59**	0.86**	0.25*
Paris	PM2.5	0.59**	0.69**	0.61**	0.60**	0.13	NA
	PM2.5abs	0.92**	0.43**	0.36**	0.36**	0.09	NA
Rome	PM2.5	0.49**	0.79**	0.91**	0.85**	0.10	NA
	PM2.5abs	0.68**	0.85**	0.71**	0.70**	0.23*	NA
Catalonia	PM2.5	0.71**	0.47**	0.50**	0.50**	0.50**	0.19**
	PM2.5abs	0.91**	0.56**	0.72**	0.72**	0.72**	0.30**
Athens	PM2.5	0.56**	0.47**	0.46**	0.27*	0.17	NA
	PM25abs	0.67**	0.38**	0.36**	0.56**	0.51**	NA
Median	PM2.5	0.53	0.47	0.52	0.53	0.22	0.27
	PM2.5abs	0.68	0.38	0.48	0.58	0.37	0.27

NA - Σhopanes/steranes not measured

NM – no model possible for organic component

** p value < 0.01

* p value < 0

Discussion

We developed LUR models for PAH, EC, OC and Σhopanes/steranes in ten study areas across Europe. LUR models were developed with high (EC), moderate (OC, ΣPAH) and low (Σhopanes/steranes) explained variance. For EC explained variance of the models was high in all study areas. For the other components large differences were found in levels of explained variance. Correlations between predictions of the newly developed LUR PM component models with model predictions for PM2.5, PM2.5absorbance varied between components and areas. EC and PAH model predictions correlated moderately to highly with especially

PM2.5 absorbance. OC model predictions correlated highest with PM2.5 model predictions.

EC models

The explained variability for EC was the same ($R^2=87\%$) as the R^2 reported previously for PM2.5 absorbance for the same study areas (Eeftens et al. 2012a) and higher than for the NO_x and PM2.5 models ($R^2=80\%$ and 74% , respectively). EC model predictions correlated high with the PM2.5 absorbance model predictions (median R^2 0.68 and 0.72, respectively). Predictor variables were similar though not identical as in the absorbance models. The high correlations between absorbance and EC model predictions is consistent with those of the measurements (Jedynska et al. 2014). Traffic-related pollutants can be modeled effectively with land use regression models, because availability of traffic intensity and-or road category and length data representing source strength is relatively good (e.g. compared to wood burning); traffic emissions are emitted at low height and traffic emission factors are relatively homogeneous (e.g. compared to industrial emissions). In our study, we further overrepresented traffic sites (35-50% of the all sites) because of prior evidence that motorized traffic was an important source of intra-urban spatial variation. Previous studies have also generally reported high explained variances for models for EC or surrogates of EC (Hoek et al. 2008). In some areas more moderate explained variances were reported, e.g. in Vancouver, attributed to the impact of difficult to characterize wood burning emissions (Hoek et al. 2008).

OC and PAH models

The lower explained variance of the OC and PAH (ΣPAH , B[a]P, chrysene) models compared to EC is probably due to the contribution of less well characterized sources in addition to traffic to OC and PAH concentrations. In the NPACT study, cross-validation R^2 values for the spatial part of intra-urban spatiotemporal models were higher for EC than for OC (0.81 versus 0.56 for the six cities combined). One PAH LUR model was previously reported for daily PAH concentrations in Fresno, California (Noth et al. 2011). The spatiotemporal model included length of highway in a 500m buffer, proximity to roads and neighborhood use of gas for heating as spatial variables, in addition to temporal weather data. The authors reported an index of agreement (which can range from 0 to 100%) of 67% suggesting overall good fit of the PAH models.

In most of our models traffic variables were included but OC and PAH have multiple sources including wood burning and industrial emissions (Jedynska et al. 2014). OC further includes both primary and secondary organic components (Saarikoski et al. 2008). Land use regression models cannot represent atmospheric formation processes well, hence the secondary component of OC was not accounted for. We did not have detailed information on sources such as wood

burning and industrial emissions available. Non-traffic sources were represented by more general variable such as: population density or industrial land use. The available industrial land use data does not include type of industry, e.g. steel and metal industry which is one of the PAH sources. The limited number of monitoring sites in the direct neighborhood of industry further contributed to the limited inclusion of industry in our models. For most study areas, industry was present within 5000 m buffers for the majority of sites, but in buffers of 1000m and smaller no industry was present for a large fraction of sites. Consistently, in the three models with industry, the 5000 m buffer was included. Identification of large industrial point sources and better databases incorporating type of industry and stack height of emissions may be needed.

We previously observed lower explained variance of LUR models for elements with significant non-traffic sources (e.g. potassium, silica, sulfur) compared to elements for which traffic is the dominant source (copper, iron) (de Hoogh et al. 2013). The moderate explained variance was attributed as well to lack of variables describing specific sources of the elements but also to low intra-urban contrasts in elemental concentrations (de Hoogh et al. 2013). The latter explanation did not apply to our OC and PAH observations. The three previous LUR studies on modeling of wood smoke also recognized the problem of obtaining good data on the spatial distribution of wood burning emissions (Smargiassi et al. 2012, Su et al. 2008, Larson et al. 2007). In the Seattle and Vancouver studies, neighborhood data from property databases was used (Su et al. 2008, Larson et al. 2007). In the Montreal study, chimney density was used as a proxy for wood burning (Smargiassi et al. 2012). The three studies reported only moderate levels of explained variance – 57% in Seattle (Larson, Henderson & Brauer 2009, Su et al. 2008), 58% in Vancouver (Su et al. 2008, Larson et al. 2007) and 40% for the global model in Montreal (Smargiassi et al. 2012).

Representation of traffic predictors

The most common representations are road length and traffic intensity (load) in buffers and distance to a (major) road. We also used the product of traffic intensity and inverse distance, because this combined variable better represents the processes of emission and dispersion than separate traffic intensity and distance variables (Hoek et al. 2010). The combined variables were included in only few models, possibly due to insufficient quality of the variables derived from GIS e.g. distance (Hoek et al. 2010).

Several LUR models included both traffic intensity and road length variables, though typically not at the same scale. Because of concern about the completeness and quality of traffic intensity data, we offered both traffic load and road length in model development. Traffic load is more specific. The inclusion of traffic intensity in many models suggests quality was sufficient in most study areas. Road length represents traffic emissions but also emissions related to population,

which may explain that mixed models performed reasonably well for urban background sites as well.

Differences between study areas

We found substantially larger differences in model R^2 between study areas for OC and PAH compared to EC. Model performance and structure may differ because of variability in measured concentrations, size and complexity of the study area, completeness and quality of predictor variables, quality of geo-coding and availability of predictor variables representing the major source of a component (Beelen et al. 2013, de Hoogh et al. 2013). On average, the models with the lowest R^2 were found in Helsinki and Copenhagen. The lack or poor performance of models for PAH and OC may be due to a smaller influence of motorized traffic emissions relative to other sources. No difference in measured PAH concentrations between street and urban background locations was found in these two cities only (Jedynska et al. 2014). The OC models for these two cities were the only models without traffic predictors. As discussed before, sources other than traffic were less well represented by variables used during LUR models development. The high R^2 in London and Paris may be due to the larger diversity in the study areas incorporating two very large cities and smaller towns. The moderate model R^2 for Catalonia could be due to the limited availability of traffic intensity data for the cities outside Barcelona (Beelen et al. 2013).

Performance at street and background sites

The generally better performance of models for street compared to urban background locations is likely due to the higher contrast of concentrations at street locations and better representation of the source. The overall model is affected heavily by the street locations. In studies with more sampling sites, investigators have built models separately for the background and local scale (Hoek et al. 2008). Relatively poor models for particularly the urban background sites were often related to models with a single predictor; models with predictors with a sizable (>50%) number of zero values e.g. natural land in small buffers; models with predictors largely restricted to major roads such as traffic load in 50 meter buffers. We included predictors with at least five non-zero observations, but could have been more restrictive.

Hopanes/steranes models

Although traffic is the main source for hopanes/steranes, we found relatively low level of explained variance (median $R^2 = 38\%$). The low model R^2 might be caused by low within study area contrast in hopanes/steranes concentrations, as indicated by the relatively low street to urban background ratio of 1.31 at the monitoring sites (Jedynska et al. 2014). In Catalonia where the concentration contrast was highest, traffic related variables were not included in the Σ hopanes/steranes model,

possibly because the traffic variables we used do not describe motor oil emission. Taken together, hopanes /steranes do not contribute much to additional characterization of human exposure of particulate matter air pollution.

Strengths and limitations

The advantage of our study was the standardization of every stage of the project. Annual averages of the pollutants used for LUR models development were obtained according to standardized protocols across all study areas. LUR models were developed centrally according to a standardized protocol. This allowed us to obtain comparable LUR models in ten European study areas for various pollutants. Care must be taken if using some of the poorer LUR models in health studies, for example by incorporating the cross validation R^2 in a sensitivity analysis. Also use of models with high R^2 , but giving predicted values which correlate highly with other pollutants (e.g. EC vs PM_{2.5} or NO_x) must be evaluated carefully in order to distinguish health effects caused by the pollutant of interest.

A limitation of our study was the lack of specific GIS variables for especially industry or wood smoke. More specific GIS data for these sources are difficult to obtain. We evaluated source-specific emission data in some areas, but these did not explain variation over the available GIS variables, probably because of a too-large spatial scale.

A further limitation of our study was the small number of sites available in the study areas for the LUR model development. It has been reported that small number of site selected for LUR models development can cause overestimation of results of models validation used in our study (LOOCV) (Basagaña et al. 2012, Wang et al. 2013). Since we had only one measurement per season we could not develop reliable models for each season.

Application in epidemiology

Though EC model performance was good in all areas, predictions of the EC models correlated highly with the predictions from the PM_{2.5} absorbance models which have already been applied in ESCAPE epidemiological studies. In most study areas, the squared correlation was above 0.5 ($\sim R=0.7$), used as a rule of thumb to determine whether the independent effect of two pollutants can be assessed (Wang et al. 2014). Though application of model predicted EC in epidemiological studies likely will result in similar associations with health as the model predicted PM_{2.5} absorbance, there may be some benefit of applying EC models to compare with previous US studies that have used EC as a metric (Vedal et al. 2013). Furthermore, as EC to absorbance concentration ratios varied across study areas (Supplementary information Table S8), effect estimates could be more homogenous between studies, if EC is associated more closely with health than PM_{2.5} absorbance.

Model performance was moderate for OC and the correlations of OC model predictions with the prediction of mostly traffic-related PM_{2.5} absorbance were moderate overall. Correlations of OC with PM_{2.5} were higher, but still moderate and highly variable across study areas. In six areas the squared correlation was below 0.5. Depending on the locations of cohort studies, OC may be a useful additional indicator. In the NPACT study, some associations between OC and cardiovascular morbidity were found (Vedal et al. 2013).

Performance of PAH models was also moderate and their predictions correlated on average moderately with PM_{2.5} absorbance and PM_{2.5} predictions with very high variation of the correlations across study areas. Application in epidemiological studies will depend on the locations of cohorts. PAH have been implicated as causal agents for lung cancer and non-malignant respiratory disease and not merely as another indicator for traffic tailpipe emissions (Noth et al. 2011).

Associated content

Supporting information

Additional information containing: (1) Map with 10 European study areas, (2) description of predictor variables, (3) Spearman correlation between B[a]P, chrysene and traffic and wood smoke markers, (4) mean and contrast of annual averages of organics components for 10 European study areas, (5) description of land use regression model for Σ PAH, (6) description of land use regression model for chrysene (7) description of land use regression model for Σ hopanes/steranes, (8) average of the model R² and LOOCV R² for EC, OC, B[a]P, Σ PAH and chrysene per study area, (9) linear regression between EC and PM_{2.5} absorbance for 10 study areas, (10) graph of measured vs modelled concentration of presented pollutants. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Appendix

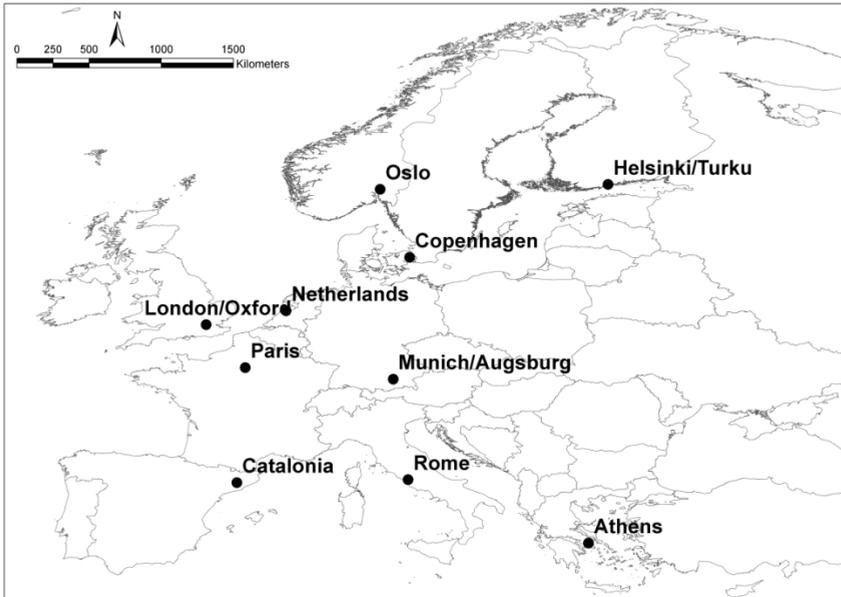


Figure S1. Map of 10 European study areas

Table S1. Predictor variables with predefined variable names, units, defined buffer sizes, transformations of the predictor variables and directions of effect.

GIS dataset	Predictor variable	Name variable ¹	Unit	Buffer size (radius in m)	Direction of effect	Central / local data
Background variables						
CORINE	Surface area of high density residential land	HDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of low density residential land	LDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Sum of high density and low density residential land	HLDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of industry	INDUSTRY_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of port	PORT_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of urban green ²	URBGREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Surface area of semi-natural and forested areas ³	NATURAL_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Sum of Urban green and Semi-natural and forested areas	GREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
Local land use	Similar to CORINE variables	Similar to CORINE variables	m ²	100, 300, 500, 1000, 5000	As CORINE	Local
Local land use	Surface area / number of buildings	BUILDINGS_X	m ² / N(umber)	100, 300, 500, 1000, 5000	+	Local
Local land use	Surface area of water	WATER_X	m ²	100, 300, 500, 1000, 5000	-	Local
Population density	Number of inhabitants	POP_X	N(umber)	100, 300, 500, 1000, 5000	+	Central / Local
Household density	Number of households	HHOLD_X	N(umber)	100, 300, 500, 1000, 5000	+	Local
Altitude	Altitude	SQRALT	m	NA	-	Local
-	Regional estimate ⁴	REGIONALESTIMATE	NA	NA	NA	Local
-	Coordinate variables ⁴	XCOORD, YCOORD or other combinations	m	NA	NA	Local
Traffic variables						
Central road network	Road length of all roads in a buffer	ROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central
Central road	Road length of major roads in a buffer ⁵	MAJORROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central

network									
Central road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEARC1 DISTINVNEARC2	m^{-1}, m^{-2}	NA	+			Central	
Central road network	Inverse distance and inverse squared distance to the nearest major road ⁵	DISTINVMAJORC1 DISTINVMAJORC2	m^{-1}, m^{-2}	NA	+			Central	
Local road network	Traffic intensity on nearest road	TRAFNEAR	Veh.day ⁻¹	NA	+			Local	
Local road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEAR1 DISTINVNEAR2	m^{-1}, m^{-2}	NA	+			Local	
Local road network	Product of traffic intensity on nearest road (TRAFNEAR) and inverse distance to nearest road (DISTINVNEAR1) and distance squared (DISTINVNEAR2)	INTINVVDIST INTINVVDIST2	Veh.day ⁻¹ m ⁻¹ Veh.day ⁻¹ m ⁻²	NA	+			Local	
Local road network	Traffic intensity on nearest major road ⁶	TRAFMAJOR	Veh.day ⁻¹	NA	+			Local	
Local road network	Inverse distance and inverse squared distance to the nearest major road ⁶	DISTINVMAJOR1 DISTINVMAJOR2	m^{-1}, m^{-2}	NA	+			Local	
Local road network	Product of traffic intensity on nearest major road (TRAFMAJOR) and inverse of distance to the nearest major road (DISTINVMAJOR1) and distance squared (DISTINVMAJOR2) ⁶	INTMAJORINVVDIST INTMAJORINVVDIST2	Veh.day ⁻¹ m ⁻¹ Veh.day ⁻¹ m ⁻²	NA	+			Local	
Local road network	Total traffic load of major roads in a buffer (sum of (traffic intensity * length of all segments)) ⁶	TRAFMAJORLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+			Local	
Local road network	Total traffic load of all roads in a buffer (sum of (traffic intensity * length of all segments))	TRAFLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+			Local	
Local road network	Heavy-duty traffic intensity on nearest road	HEAVYTRAFNEAR*	Veh.day ⁻¹	NA	+			Local	
Local road network	Product of heavy-duty traffic	HEAVYINTINVVDIST	Veh.day ⁻¹ m ⁻¹	NA	+			Local	

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network	intensity on nearest road (HEAVYINT) and inverse of distance to the nearest road (INVDIST) and distance squared (INVDIST2)	HEAVYINTINVDIST2	Veh.day ⁻¹ m ⁻²			
Local road network	Heavy-duty traffic intensity on nearest major road ⁶	HEAVYTRAFMAJOR	Veh.day ⁻¹	+	NA	Local
Local road network	Total heavy-duty traffic load of major roads in a buffer (sum of heavy-duty traffic intensity * length of all segments) ⁶	HEAVYTRAFMAJORLOAD_X	Veh.day ⁻¹ m	+	25, 50, 100, 300, 500, 1000	Local
Local road network	Total heavy-duty traffic load of all roads in a buffer (sum of heavy-duty traffic intensity * length of all segments)	HEAVYTRAFLOAD_X	Veh.day ⁻¹ m	+	25, 50, 100, 300, 500, 1000	Local

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Table S2. Spearman correlation between B[a]P, chrysene and traffic and wood smoke marker.

Study area	PAH	NOx	EC	levoglucosan
Oslo	chrysene	0.79	0.87	0.84
	B[a]P	0.77	0.85	0.88
Helsinki/Turku	chrysene	0.24	0.64	
	B[a]P	0.13	0.56	
Copenhagen	chrysene	0.03	0.14	
	B[a]P	0.00	0.14	
London/Oxford	chrysene	0.73	0.74	
	B[a]P	0.49	0.57	
Netherlands	chrysene	0.47	0.50	0.62
	B[a]P	0.44	0.51	0.66
Munich/Augsburg	chrysene	0.75	0.75	0.19
	B[a]P	0.46	0.50	0.51
Paris	chrysene	0.81	0.86	
	B[a]P	0.78	0.87	
Rome	chrysene	0.77	0.77	
	B[a]P	0.69	0.63	
Catalonia	chrysene	0.78	0.77	0.07
	B[a]P	0.59	0.59	0.32
Athens	chrysene	0.40	0.54	
	B[a]P	0.65	0.56	
Median	chrysene	0.74	0.75	0.41
	B[a]P	0.54	0.56	0.58

Table S3. Mean and contrast of annual averages for 10 European study areas

Study area	n	OC			EC			ΣPAH			B[a]P			Σhopanes/steranes		
		Mean ($\mu\text{g}/\text{m}^3$)	Range	R/M (%)	Mean ($\mu\text{g}/\text{m}^3$)	Range	R/M (%)	Mean (ng/m^3)	Range	R/M (%)	Mean (ng/m^3)	Range	R/M (%)	Mean (ng/m^3)	Range	R/M (%)
Oslo	19	1.7	3.3	199	1.0	2.0	200	1.2	3.3	280	0.14	0.41	292	2.3	2.8	124
Helsinki/Turku	20	1.1	2.0	189	0.8	2.1	254	1.8	3.3	183	0.17	0.39	221	N/A	N/A	N/A
Copenhagen	20	1.5	2.1	141	1.0	1.2	124	2.1	5.7	276	0.21	0.75	352	N/A	N/A	N/A
London/Oxford	20	1.4	3.1	220	1.3	5.3	399	1.0	2.7	276	0.09	0.31	354	N/A	N/A	N/A
Netherlands	16	1.8	1.9	107	1.2	1.4	115	1.4	2.8	200	0.14	0.27	189	2.8	3.7	135
Munich/Augsburg	20	2.7	3.1	117	1.5	2.2	149	1.3	2.0	157	0.13	0.24	178	2.2	2.0	91
Paris	20	2.2	5.5	244	1.8	7.6	420	1.5	4.0	256	0.14	0.44	307	N/A	N/A	N/A
Rome	20	3.7	3.1	84	2.3	2.6	115	2.0	3.7	183	0.19	0.43	222	N/A	N/A	N/A
Catalonia	40	2.8	5.8	210	2.2	4.8	222	1.6	2.8	179	0.17	0.35	204	5.0	14.9	297
Athens	20	3.5	4.3	121	1.6	2.9	177	2.0	3.9	196	0.25	0.65	266	N/A	N/A	N/A
R/M Range/Mean																
N/A not analysed																

Table S4. Description of land use regression model for ΣPAH (ng/m³)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE (ng/m ³)	Measured concentration (ng/m ³)
Oslo	$1.227 + 7.297 \times 10^{12} \times \text{TRAFLOAD}_{1000} - 0.0580 \text{ SQRALT}$	19	71	58	0.526	1.18 [0.06 - 3.36]
Helsinki/Turku*	-	20				1.78 [0.51 - 3.77]
Copenhagen*	-	20				2.08 [0.69 - 6.43]
London/Oxford	$0.957 + 78.388 \times \text{DISTINVMajorC2} - 4.911 \times 10^{-8} \times \text{NATURAL}_{5000} - 1.942 \times 10^{-8} \times \text{URBGREEN}_{5000} + 0.00000503 \times \text{TRAFMAJOR} + 0.000741 \times \text{MAJORROADLENGTH}_{100}$	20	93	89	0.175	0.98 [0.23 - 2.93]
Netherlands	$1.621 + 0.0061 \times \text{MAJORROADLENGTH}_{50} - 5.429 \times 10^{-8} \times \text{UGNL}_{5000}$	16	58	31	0.511	1.40 [0.44 - 3.24]
Munich/Augsburg**	$1.030 + 0.00224 \times \text{MAJORROADLENGTH}_{100}$	20	31	9	0.430	1.25 [0.48 - 2.43]
Paris**	$0.380 + 0.000214 \times \text{MAJORROADLENGTH}_{500} + 2.649 \times 10^{-8} \times \text{LDRES}_{5000} - 5.850 \times 10^{-8} \times \text{URBGREEN}_{5000} + 0.0000123 \times \text{LDRES}_{100}$	20	85	63	0.359	1.54 [0.48 - 4.43]
Rome	$1.226 + 19.120 \times \text{DISTINVMajor1} + 0.00153 \times \text{MAJORROADLENGTH}_{50} + 6.061 \times 10^{-8} \times \text{INDUSTRY}_{5000}$	20	84	74	0.389	2.03 [0.86 - 4.58]
Catalonia	$0.761 + 0.000228 \times \text{INTMAJORINVDIST1} + 9.957 \times 10^{-7} \times \text{HDRES}_{500}$	40	37	27	0.597	1.56 [0.28 - 3.07]
Athens**	$1.095 + 0.00897 \times \text{ROADLENGTH}_{25} + 3.470 \times 10^{-8} \times \text{TRAFLOAD}_{100}$	20	44	8	0.657	1.99 [0.95 - 4.84]
Median		65		45		

* no model possible due to an influential site. ** too high Cook's D value

Table S5. Description of land use regression models for chrysene (ng/m³)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE (ng/m ³)	Measured concentration (ng/m ³)
Oslo	$0.157 + 1.165 \times 10^{-12} \times \text{TRAFLOAD_1000} + 0.00463 \times \text{MAJORROADLENGTH_25} + 279.4 \times \text{HEAVYINTINVDIST2} - 0.0126 \times \text{SQAL T}$	19	83	65	0.0810	0.20 [0.00 - 0.58]
Helsinki/Turku	$0.169 + 0.000760 \times \text{ROADLENGTH_50}$	20	23	8	0.1116	0.25 [0.07 - 0.51]
Copenhagen*	-	20				0.34 [0.08 - 0.92]
London/Oxford	$0.0662 + 0.0000309 \times \text{HEAVYTRAFMAJOR} + 2.0342 \times \text{DISTINVMajorCI}$	20	91	89	0.0377	0.17 [0.04 - 0.56]
Netherlands	$0.286 + 0.00149 \times \text{MAJORROADLENGTH_50} - 1.162 \times 10^{-8} \times \text{UGNL_5000}$	16	71	50	0.0927	0.25 [0.07 - 0.64]
Munich/Augsburg	$0.0907 + 2.826 \times 10^{-9} \times \text{TRAFMAJORLOAD_300} + 0.000582 \times \text{MAJORROADLENGTH_50_v2}$	20	46	33	0.0739	0.17 [0.06 - 0.38]
Paris	$0.106 + 7.963 \times 10^{-9} \times \text{INDUSTRY_5000} + 1.346 \times 10^{-7} \times \text{POP_5000} - 1.439 \times 10^{-8} \times \text{URBGREEN_5000} + 4.808 \times 10^{-8} \times \text{LDRES_1000}$	19	84	73	0.0439	0.27 [0.05 - 0.97]
Rome	$0.0110 + 0.000410 \times \text{POP_100} + 6.556 \times 10^{-7} \times \text{LDRES_300} + 0.000977 \times \text{MAJORROADLENGTH_50}$	20	90	83	0.0648	0.31 [0.10 - 0.90]
Catalonia	$0.0764 + 0.0000526 \times \text{INTMAJORINVDIST1} + 1.915 \times 10^{-7} \times \text{HDRES_500}$	40	55	47	0.0893	0.24 [0.04 - 0.62]
Athens	$0.205 + 1.686 \times 10^{-8} \times \text{TRAFMAJORLOAD_25}$	19	41	30	0.0470	0.24 [0.10 - 0.64]
Median			71	50		

* no model possible due to an influential site

Table S6. Description of land use regression model for Σ hopanes/steranes (ng/m³)

Study area	LUR model	n	R ² (%)	LOOCV R ² (%)	RMSE (ng/m ³)	Measured concentration (ng/m ³)
Oslo	$1.938 + 5.456 \times 10^{-7} \times \text{PORT_5000}$	19	18	2	0.823	2.29 [1.30 - 4.13]
Netherlands	$5.750 + 28.658 \times \text{DISTINVMAJOR2} + 0.0000862 \times \text{POP_500} - 0.00000759 \times \text{YCOORD}$	16	78	63	0.519	2.75 [1.46 - 5.16]
Munich/Augsburg	$52.895 + 0.000849 \times \text{ROADLENGTH_100} + 0.000165 \times \text{INTMAJORINVDIST} - 0.0000115 \times \text{XCOORD}$	20	58	41	0.403	2.18 [1.00 - 2.98]
Catalonia	$1.081 + 0.00000190 \times \text{HDRES_1000}$	40	27	21	3.004	5.00 [1.56 - 16.4]
Median			43	31		

Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

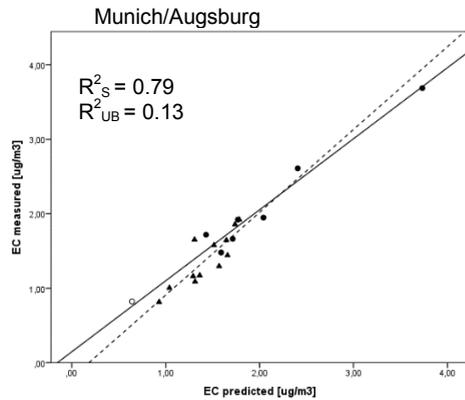
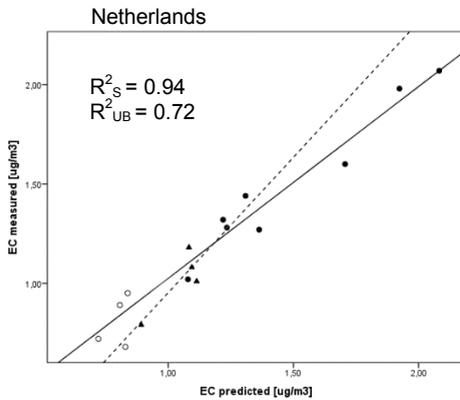
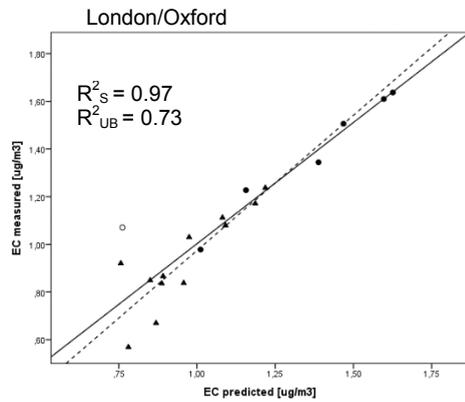
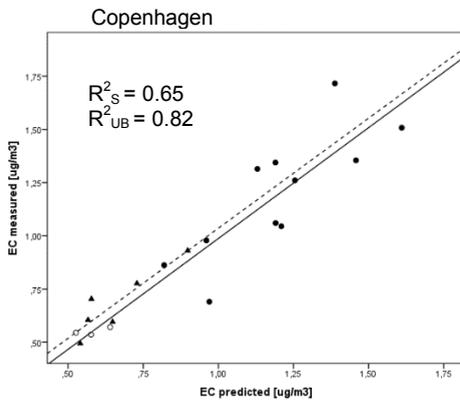
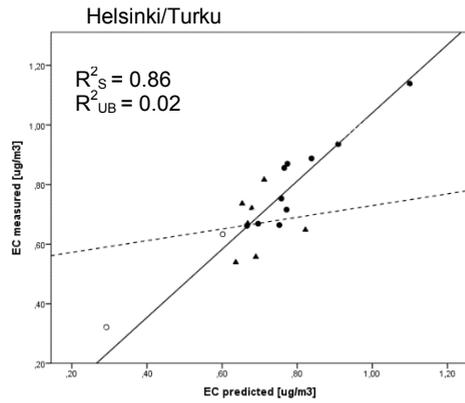
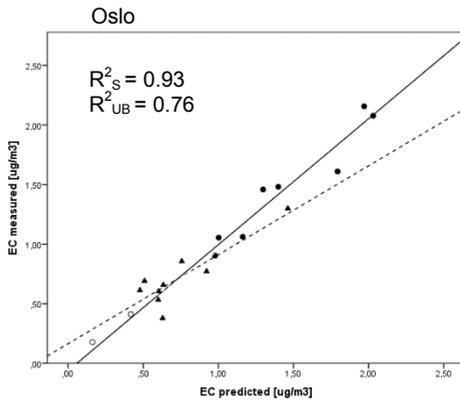
Table S7. Average of the model R² and LOOCV R² for EC, OC, B[a]P, ΣPAH and chrysene per study area

	R² (%)	LOOCV R² (%)
Oslo	76	61
Helsinki/Turku	29	22
Copenhagen	24	21
London/Oxford	87	81
Netherlands	74	56
Munich/Augsburg	51	35
Paris	86	72
Rome	71	60
Catalonia	50	40
Athens	59	43

Table S8. Linear regression between EC and PM2.5 absorbance

Study area		Regression	R²
Oslo	with intercept	EC = -0.407 + 1.061*PM2.5abs	0.894
	w/o intercept	EC = 0.789*PM2.5abs	0.960
Helsinki/Turku	with intercept	EC = -0.327 + 1.017*PM2.5abs	0.842
	w/o intercept	EC = 0.752*PM2.5abs	0.957
Copenhagen	with intercept	EC = -0.136 + 0.909*PM2.5abs	0.636
	w/o intercept	EC = 0.807*PM2.5abs	0.949
London/Oxford	with intercept	EC = -0.672 + 1.223*PM2.5	0.890
	w/o intercept	EC = 0.896*PM2.5abs	0.924
Netherlands	with intercept	EC = -0.090 + 0.819*PM2.5	0.951
	w/o intercept	EC = 0.767*PM2.5abs	0.995
Munich/Augsburg	with intercept	EC = -1.352 + 1.480*PM2.5	0.955
	w/o intercept	EC = 0.799*PM2.5	0.958
Paris	with intercept	EC = -1.342 + 1.575*PM2.5	0.908
	w/o intercept	EC = 1.039*PM2.5	0.898
Rome	with intercept	EC = -0.443 + 0.944*PM2.5	0.695
	w/o intercept	EC = 0.798*PM2.5	0.965
Catalonia	with intercept	EC = -0.668 + 1.144*PM2.5	0.832
	w/o intercept	EC = 0.904*PM2.5	0.956
Athens	with intercept	EC = -0.596 + 0.941*PM2.5	0.619
	w/o intercept	EC = 0.700*PM2.5abs	0.943

Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

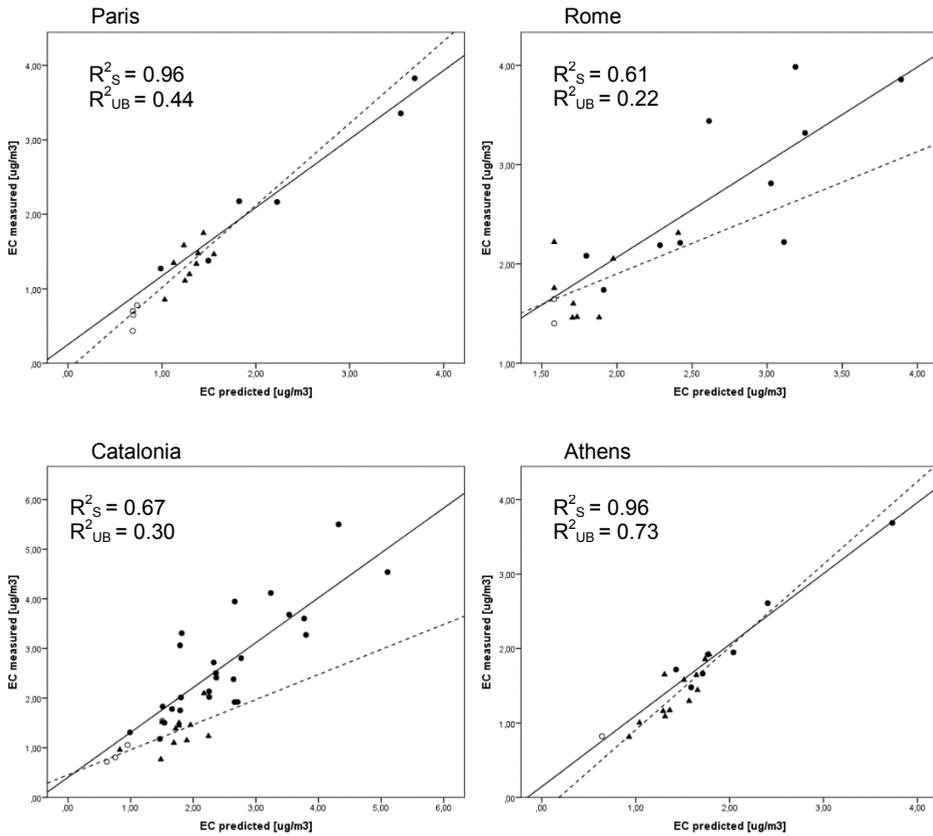
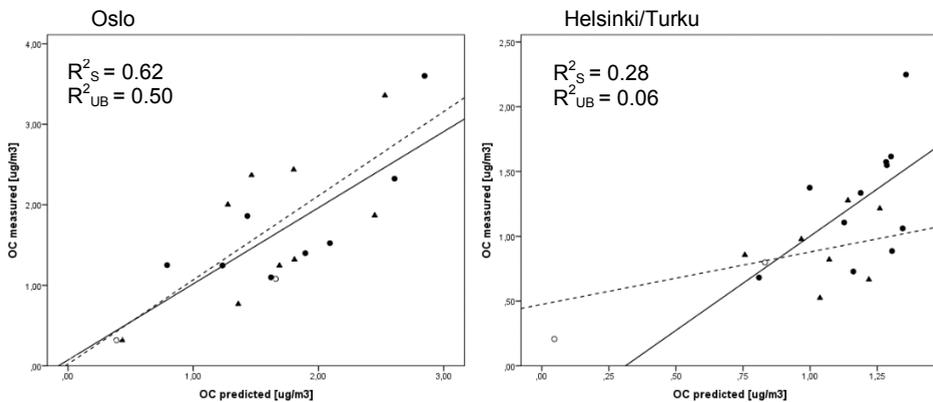
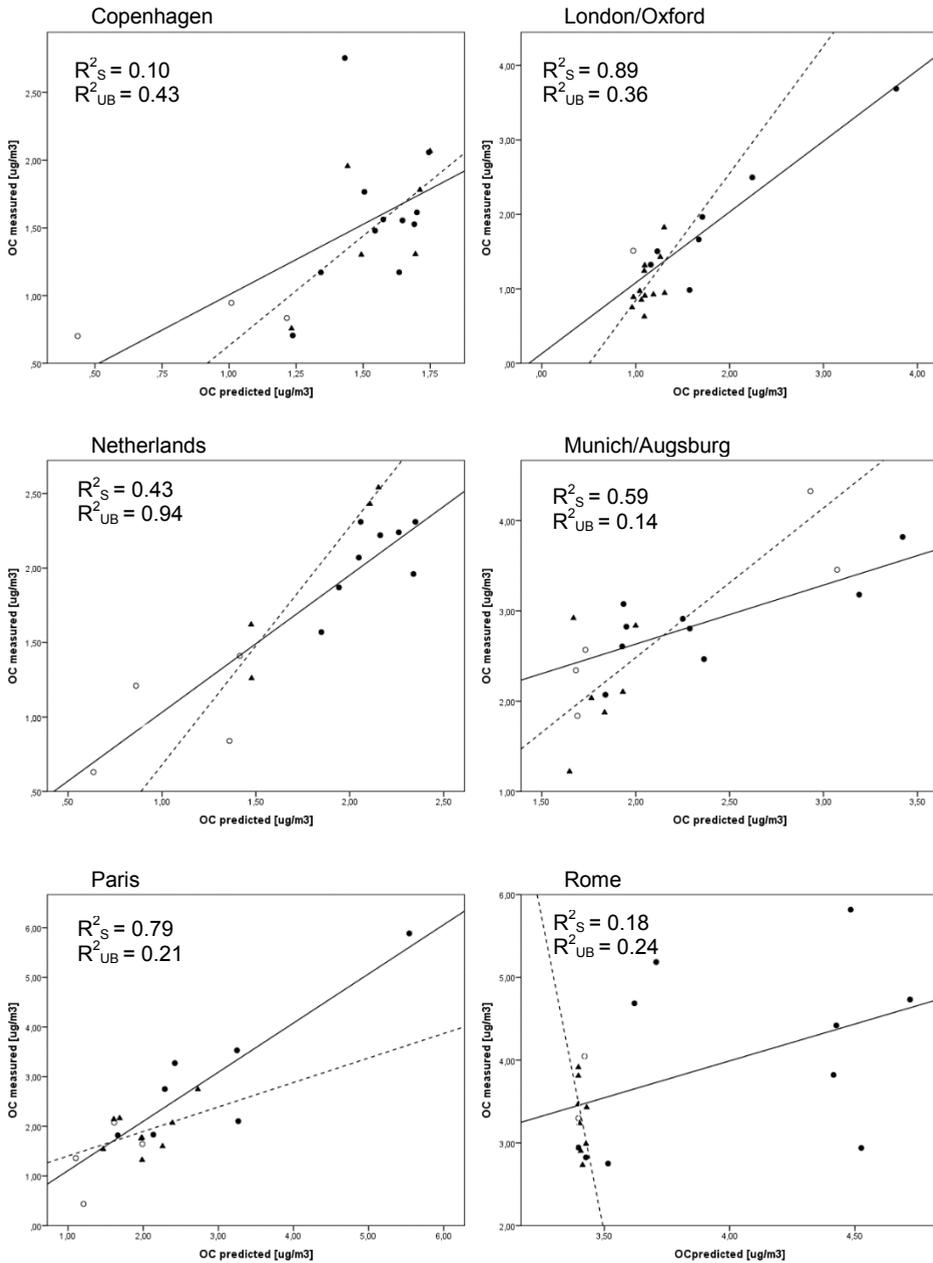


Figure S2. Correlation between measured and predicted EC annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line - UB



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

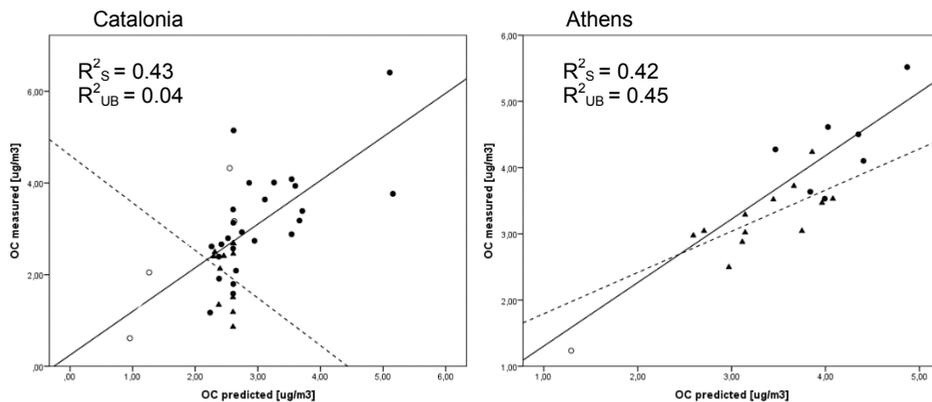
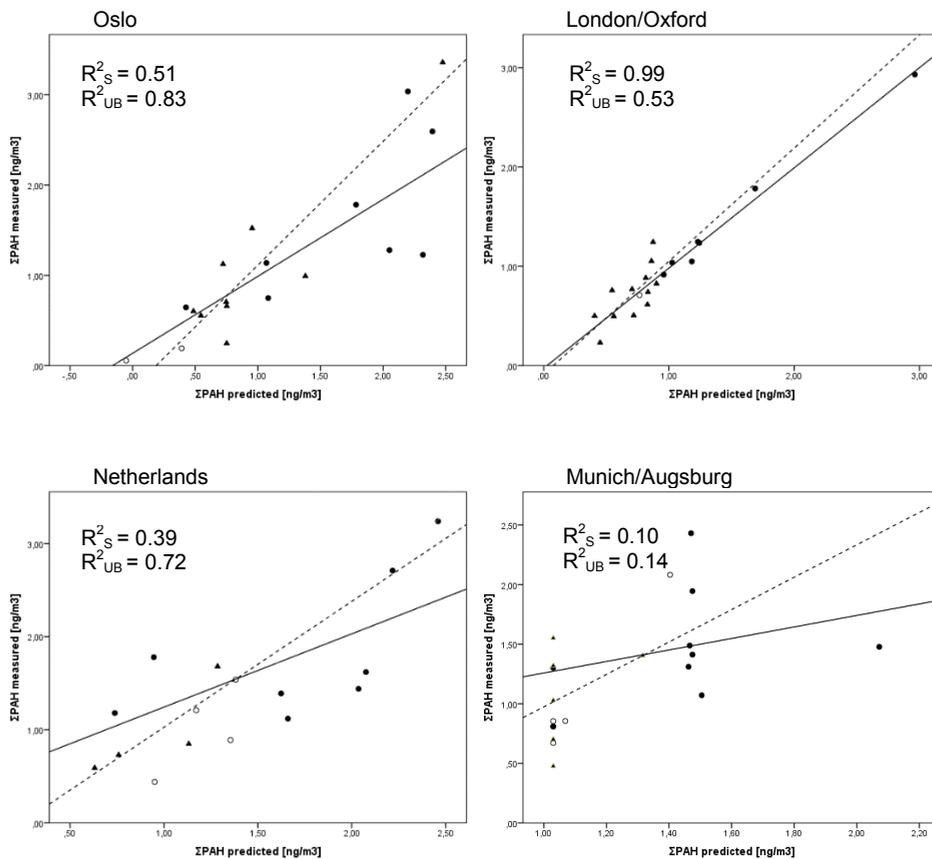


Figure S3. Correlation between measured and predicted OC annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line - UB



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

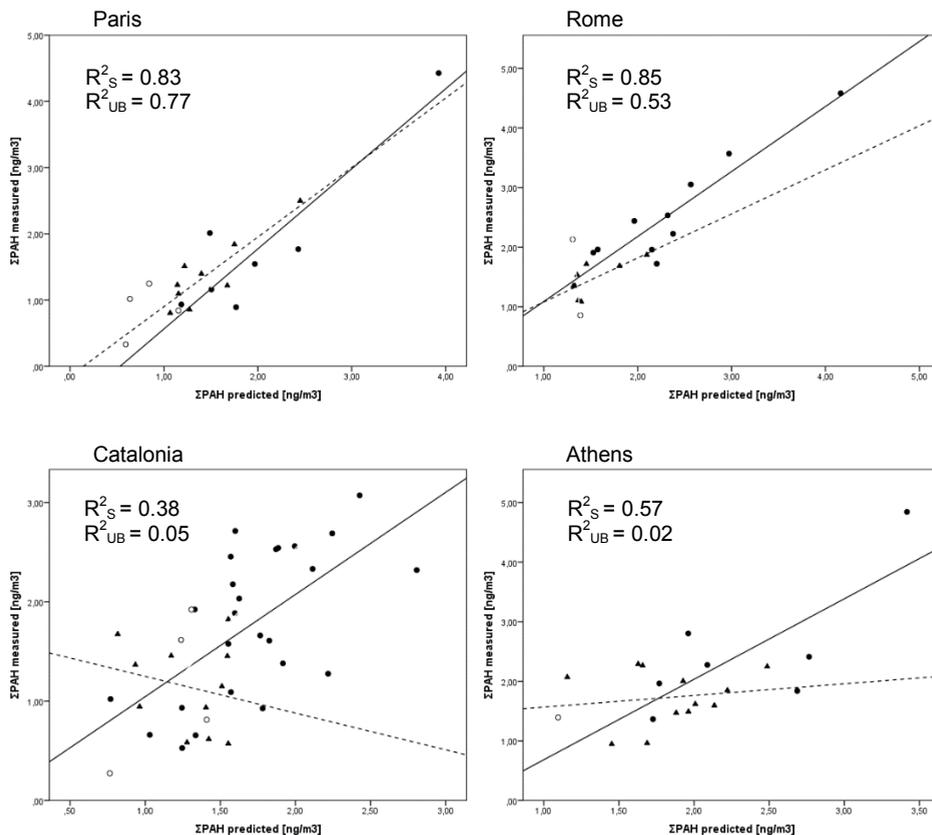
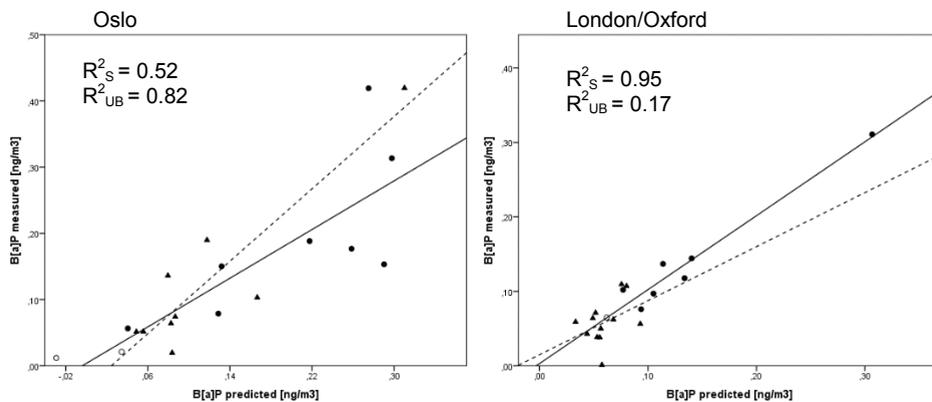


Figure S4. Correlation between measured and predicted ΣPAH annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line – UB



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

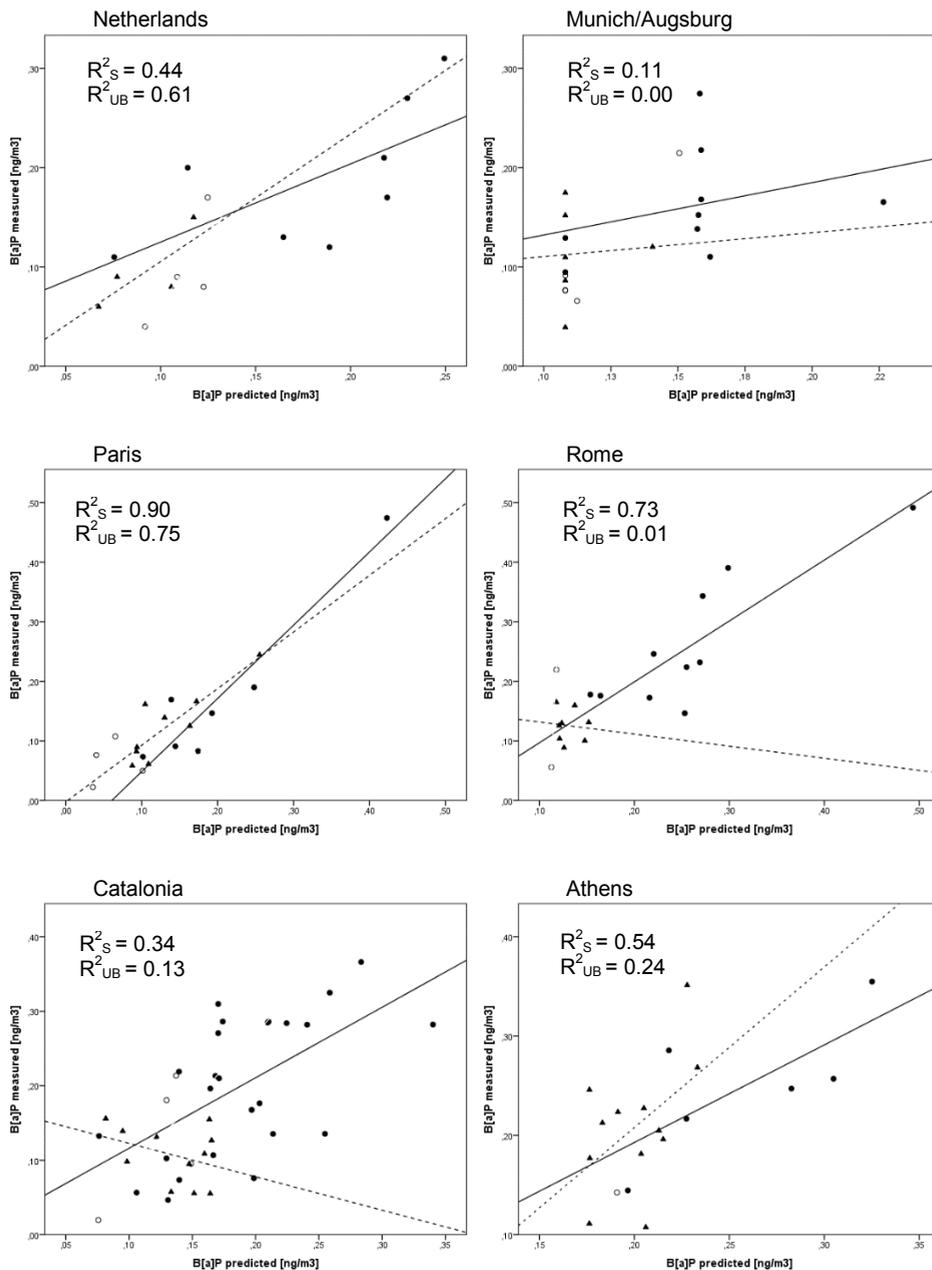
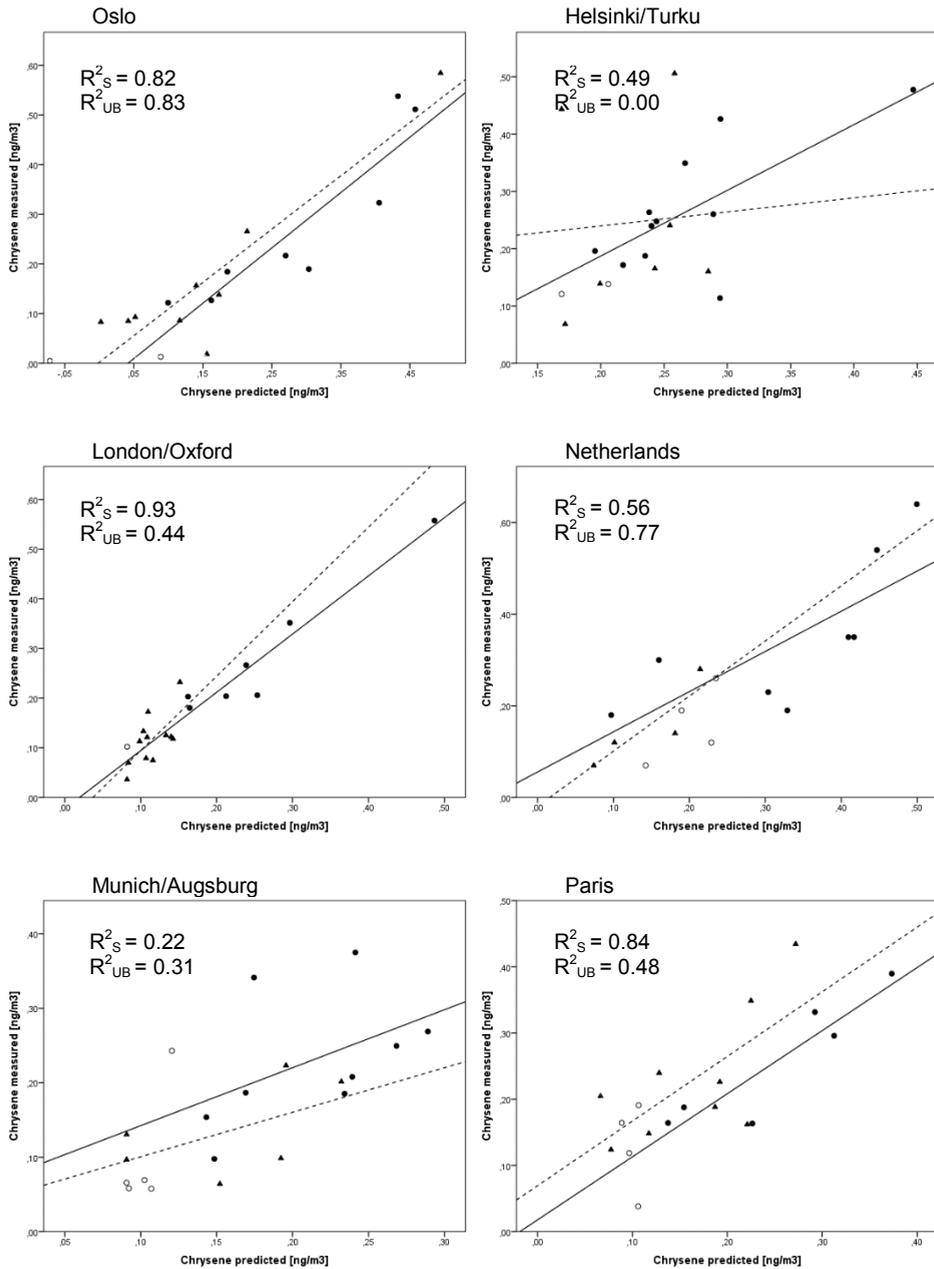


Figure S5. Correlation between measured and predicted B[a]P annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line - UB

Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

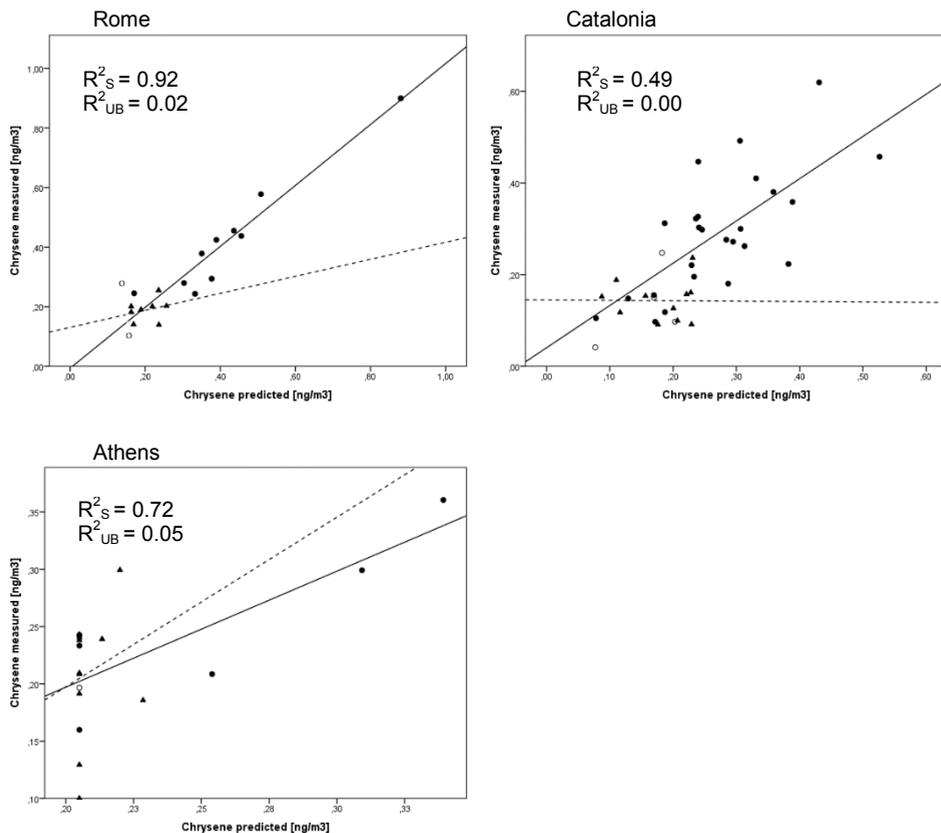
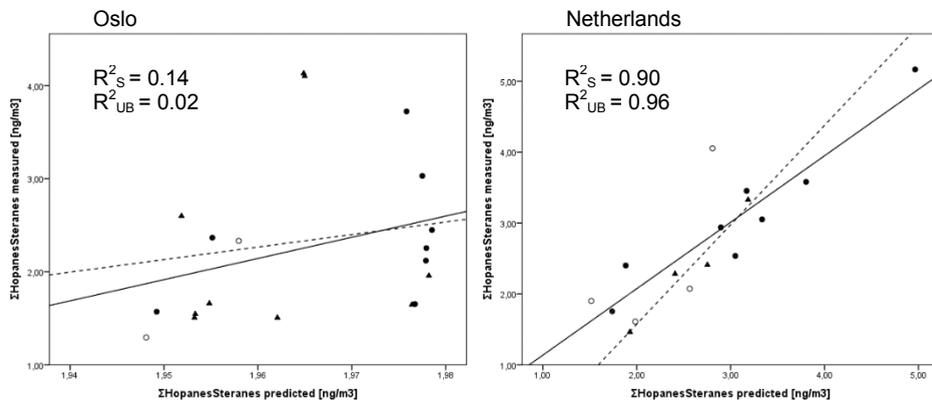


Figure S6. Correlation between measured and predicted Chrysene annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line – UB



Chapter 3: LUR models for EC/OC, PAH, and hopanes/steranes

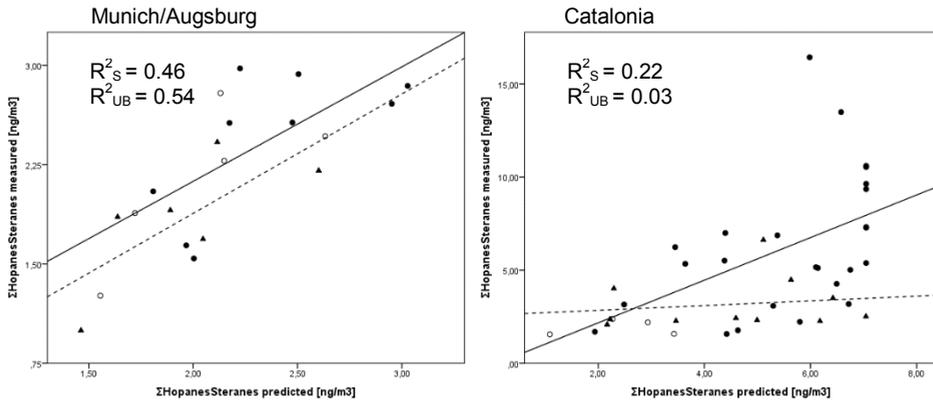


Figure S7. Correlation between measured and predicted Σ HopanesSteranes annual averages for S - ●, UB - ▲, RB - ○. Solid line – S, dotted line - UB

**Spatial variations of levoglucosan in four
European study areas**

Aleksandra Jedynska
Marloes Eeftens
Marta Cirach
Antoon Visschedijk
Kees Meliefste
Bert Brunekreef

Gerard Hoek
Josef Cyrus
Audrey De Nazelle
Wenche Nystad
Mark Nieuwenhuijsen
Ingeborg M. Kooter

Meng Wang
Rob Beelen
Menno Keuken
Helgah Makarem Akhlaghi
Kees de Hoogh

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: PM_{2.5}, PM_{2.5} absorbance, PM₁₀, 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 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: PM_{2.5}, NO_x and EC. Levoglucosan had the highest spatial correlation with Σ PAH ($r=0.65$) and the lowest with traffic markers – NO_x, Σ hopanes/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 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 R² 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 PM_{2.5} mass and traffic markers offers the potential to assess health effects of wood smoke separate from traffic-related air pollution.

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, 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, 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 PM_{2.5}, PM₁₀ and the traffic markers NO₂, 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 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: NO_x, NO₂, PM_{2.5}, PM₁₀, 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, de Hoogh et al. 2013, Eeftens et al. 2012b, Cyrus 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 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.

Methods

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 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.

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.

Analytical methods

Levoglucosan

All measurements were performed centrally at TNO. 2.5 cm² 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 silyating 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 (v_c, recovery (u_{tv}) and accuracy of the calibration standard (u_j), following the Dutch norm NEN 7777 Environment - Performance characteristics of measurement methods ($U_c = \sqrt{(v_c)^2 + (u_j)^2 + (u_{tv})^2}$). Reproducibility of our method is between 7 and 15 % depending on levoglucosan concentration in analysed samples.

EC/OC, PAH, hopanes, steranes, PM2.5, NO₂ 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, 1cm² 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 µm 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). NO₂ was measured with Ogawa passive samplers (Cyrus 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.

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, Cyrus 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).

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 (Maenhaut 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% (Maenhaut et al. 2012).

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, Cyrus et al. 2012).

At the reference sites, the following components were measured: NO_x, NO₂, PM_{2.5}, PM_{2.5} absorbance and PM₁₀. 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, PM₁₀ and PM_{coarse} in three study areas (Stockholm County, The Netherlands/Belgium and Catalonia) (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.

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 PM_{2.5}, 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).

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.

Results

The main focus of presented results is on adjusted annual average concentrations, except section 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 NO_x correlated highest with levoglucosan. NO_x was used for temporal adjustment in the Netherlands, Munich/Augsburg and Catalonia. In Oslo, due to an incomplete data set of NO_x at the reference site, we used $\text{PM}_{2.5}$ absorbance for temporal adjustment. The correlation between levoglucosan and $\text{PM}_{2.5}$ absorbance was only slightly lower than between levoglucosan and NO_x ($r=0.984$ 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).

Within and between study area contrast

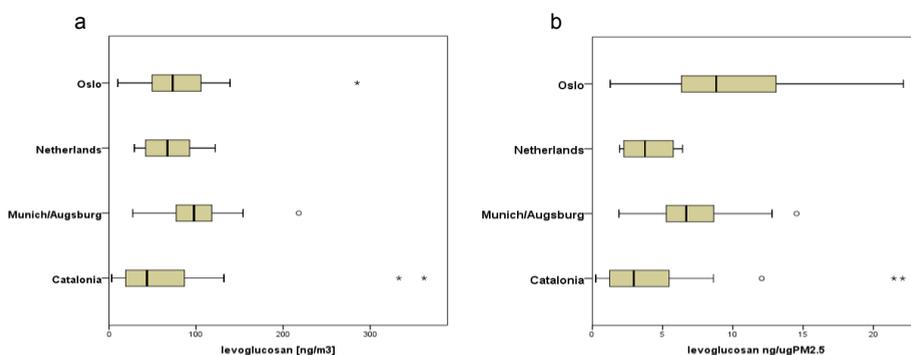


Figure 1. Distribution of the adjusted annual average concentration of levoglucosan within study areas. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. a) results in ng/m^3 , b) results in $\text{ng}/\mu\text{gPM}_{2.5}$.

Chapter 4: Spatial variations of levoglucosan

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	
						25 th	75 th
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

Levoglucosan concentrations were highest in Munich/Augsburg – 102 ng/m³ and lowest in Catalonia 64ng/m³ (Figure 1, Table 2) but the differences in levoglucosan concentrations between study areas were not statistically significant. The lack of samples taken in winter (December – February) in Munich /Augsburg may have influenced the annual average concentrations. Because of the applied correction of the concentrations for temporal variation using a continuous site, the impact is diminished. To the extent that the seasonal pattern of NO_x (used for correction) and levoglucosan differ, correction may not be sufficient. To test this, we deleted the winter samples from the Netherlands and observed that the temporally adjusted annual average changed from 70 to 60 ng/m³.

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 (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 PM_{2.5}. The highest fraction of levoglucosan in PM_{2.5} was found in Oslo (9.51 ng/μgPM_{2.5}) (Figure1b). The outliers for the fraction are the same sites as for levoglucosan concentrations per m³. 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.

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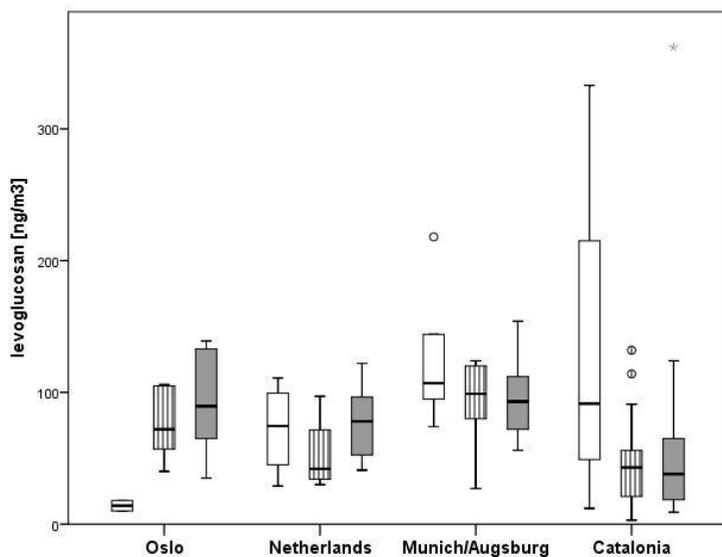


Figure 2. The adjusted annual average concentration of levoglucosan for different site types. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. White – regional background, striped – urban background, grey – street locations.

Seasonal differences

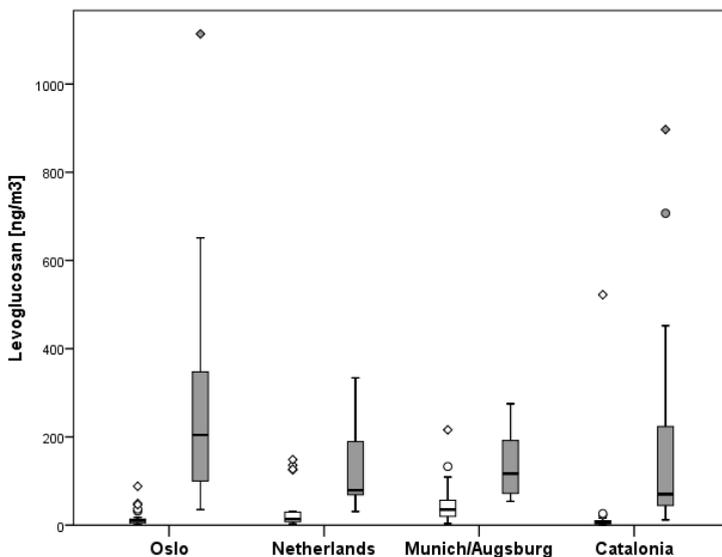


Figure 3. Seasonal differences of levoglucosan concentrations. White – warm, grey – cold season.

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.

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 Σ PAH and B[a]P with median correlation coefficients of 0.65 and 0.58, respectively. Levoglucosan – 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: Σ hopanes/steranes and NO_x (median $r = -0.22$). A relatively poor correlation was found between K in $\text{PM}_{2.5}$ and levoglucosan (median $r=0.33$). The correlation between K in PM_{10} and levoglucosan was even slightly lower (median $r= 0.27$).

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

Study area	PM2.5	PM2.5ABS	NO _x	EC	OC	Σ PAH	B[a]P	Σ hopanes/ 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 $p < 0.01$

Contribution 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 $\text{PM}_{2.5}$ 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.

Table 4. Calculated contribution of wood smoke to measured PM_{2.5} OC and mass. Calculated 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 PM_{2.5} mass.

Study area	Levoglucosan ng/m ³	Cal. OC wood smoke µg/m ³	Cal. 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

Cal. - calculated

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 β '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.

Chapter 4: Spatial variations of levoglucosan

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	59	39	40.46
Netherlands	22.72 - 0.00005213 * NATURAL_1000 + 0.0003478 * xcoord	16	60	48	20.75
Munich/Augsburg	74.88 + 148.42 * HD_LD_RES_300 - 651.46 * URBGREEN - 298.69 * NATURAL1000	20	60	36	27.69
Catalonia	-3998.2 - 0.00000617*URBGREEN_5000 - 2.92*SQRALT + 0.000885 * ycoord	38	71	62	20.27
Median			60	44	24.22

POP1000 – population in 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

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 PM_{2.5}, 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 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 R² = 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.

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 , $\text{PM}_{2.5}$ abs, EC, Σ hopanes/steranes) and $\text{PM}_{2.5}$ mass which had the highest concentrations in Barcelona (and other southern European areas) and the lowest concentrations in Oslo (and other Northern European areas) (Cyrus 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 et al. 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 et al. 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 et al. 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 (Maenhaut et al. 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 (Maenhaut 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 $480 \text{ (Graz) ng/m}^3$ (Caseiro et al. 2009). In

the UK annual average levoglucosan concentrations were low – about 9 ng/m³ (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.

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/m³) and summer (95% of samples below the detection limit of 2 ng/m³) (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).

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 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).

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 Σ PAH and B[a]P (0.51 – 0.89). Wood burning is known to be one of the PAH sources (Ravindra, Sokhi & Van Grieken 2008) The correlation with Σ PAH 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 Σ 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 versus EC, OC and PM_{2.5} (Maenhaut 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 in fire places (Puxbaum et al. 2007) (Table S6).

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 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 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 (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 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.

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}, 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 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 R² = 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.

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Chapter 4

Appendix

Table S1. Predictor variables with predefined variable names, units, defined buffer sizes, transformations of the predictor variables and directions of effect.

GIS dataset	Predictor variable	Name variable ¹	Unit	Buffer size (radius in m)	Direction of effect	Central / local data
Background variables						
CORINE	Surface area of high density residential land	HDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of low density residential land	LDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Sum of high density and low density residential land	HLDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of industry	INDUSTRY_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of port	PORT_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of urban green ²	URBGREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Surface area of semi-natural and forested areas ³	NATURAL_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Sum of Urban green and Semi-natural and forested areas	GREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
Local land use	Similar to CORINE variables	Similar to CORINE variables	m ²	100, 300, 500, 1000, 5000	As CORINE	Local
Local land use	Surface area / number of buildings	BUILDINGS_X	m ² / N(umber)	100, 300, 500, 1000, 5000	+	Local
Local land use	Surface area of water	WATER_X	m ²	100, 300, 500, 1000, 5000	-	Local
Population density	Number of inhabitants	POP_X	N(umber)	100, 300, 500, 1000, 5000	+	Central / Local
Household density	Number of households	HHOLD_X	N(umber)	100, 300, 500, 1000, 5000	+	Local
Altitude	Altitude	SQRALT	m	NA	-	Local
-	Regional estimate ⁴	REGIONALESTIMATE	NA	NA	NA	Local
-	Coordinate variables ⁴	XCOORD, YCOORD or other combinations	m	NA	NA	Local
Traffic variables						
Central road network	Road length of all roads in a buffer	ROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central
Central road	Road length of major roads in a buffer ⁵	MAJORROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central

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network									
Central road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEARC1 DISTINVNEARC2	m^{-1}, m^{-2}	NA	+			Central	
Central road network	Inverse distance and inverse squared distance to the nearest major road ⁵	DISTINVMAJORC1 DISTINVMAJORC2	m^{-1}, m^{-2}	NA	+			Central	
Local road network	Traffic intensity on nearest road	TRAFNEAR	$Veh.day^{-1}$	NA	+			Local	
Local road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEAR1 DISTINVNEAR2	m^{-1}, m^{-2}	NA	+			Local	
Local road network	Product of traffic intensity on nearest road (TRAFNEAR) and inverse distance to nearest road (DISTINVNEAR1) and distance squared (DISTINVNEAR2)	INTINVVDIST INTINVVDIST2	$Veh.day^{-1}m^{-1}$ $Veh.day^{-1}m^{-2}$	NA	+			Local	
Local road network	Traffic intensity on nearest major road ⁶	TRAFMAJOR	$Veh.day^{-1}$	NA	+			Local	
Local road network	Inverse distance and inverse squared distance to the nearest major road ⁶	DISTINVMAJOR1 DISTINVMAJOR2	m^{-1}, m^{-2}	NA	+			Local	
Local road network	Product of traffic intensity on nearest major road (TRAFMAJOR) and inverse of distance to the nearest major road (DISTINVMAJOR1) and distance squared (DISTINVMAJOR2) ⁶	INTMAJORINVDIST INTMAJORINVDIST2	$Veh.day^{-1}m^{-1}$ $Veh.day^{-1}m^{-2}$	NA	+			Local	
Local road network	Total traffic load of major roads in a buffer (sum of (traffic intensity * length of all segments)) ⁶	TRAFMAJORLOAD_X	$Veh.day^{-1}m$	25, 50, 100, 300, 500, 1000	+			Local	
Local road network	Total traffic load of all roads in a buffer (sum of (traffic intensity * length of all segments))	TRAFLOAD_X	$Veh.day^{-1}m$	25, 50, 100, 300, 500, 1000	+			Local	
Local road network	Heavy-duty traffic intensity on nearest road	HEAVYTRAFNEAR*	$Veh.day^{-1}$	NA	+			Local	
Local road network	Product of heavy-duty traffic intensity on nearest road (HEAVYINT) and inverse of distance to the nearest road (INVDIST) and distance squared	HEAVYINTINVDIST HEAVYINTINVDIST2	$Veh.day^{-1}m^{-1}$ $Veh.day^{-1}m^{-2}$	NA	+			Local	

	(INVDIST2)							
Local road network	Heavy-duty traffic intensity on nearest major road ⁶	HEAVYTRAFMAJOR	Veh.day ⁻¹	NA	+		Local	
Local road network	Total heavy-duty traffic load of major roads in a buffer (sum of (heavy-duty traffic intensity * length of all segments)) ⁶	HEAVYTRAFMAJORLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+		Local	
Local road network	Total heavy-duty traffic load of all roads in a buffer (sum of (heavy-duty traffic intensity * length of all segments))	HEAVYTRAFLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+		Local	

Chapter 4: Spatial variations of levoglucosan

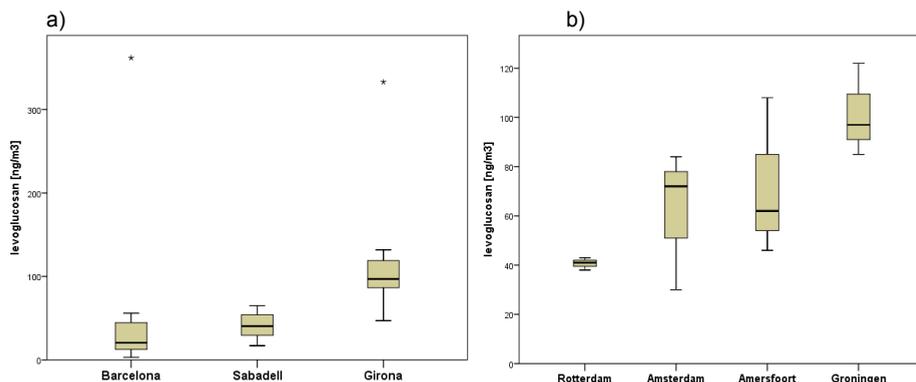


Figure S1. Distribution of the adjusted year average concentration of levoglucosan within study areas. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown. a) Catalonia, from south to north b) The Netherlands, from west to east.

Table S2: List of components used for temporal correction of levoglucosan with median Pearson temporal correlation (r)

Study area	Component	median r
Oslo	PM2.5abs	0.987
Netherlands	NOx	0.916
Munich/Augsburg	NOx	0.996
Catalonia	NOx	0.980

r is the correlation between measurements of levoglucosan at a measurement site and the standard component measured at the reference site (e.g. PM2.5 absorbance for Oslo). Correlations are calculated per site and thus reflect the temporal correlation. The median of site-specific individual correlation coefficients are calculated and presented in the table.

Table S3: Pearson correlation (r) between unadjusted and ratio-adjusted concentrations of levoglucosan

Study area	r
Oslo	0.97
Netherlands	0.94
Munich/Augsburg	0.94
Catalonia	0.93

Table S4. Difference of levoglucosan annual concentrations between site types (ratios RB/UB and S/UB)

Study area	n	RB/UB	S/UB
Oslo	19	0.15	0.99
Netherlands	16	1.37	1.46
Munich/Augsburg	20	1.39	1.04
Catalonia	40	2.63*	1.19

*Significant difference between site types with $p < 0.01$

Chapter 4: Spatial variations of levoglucosan

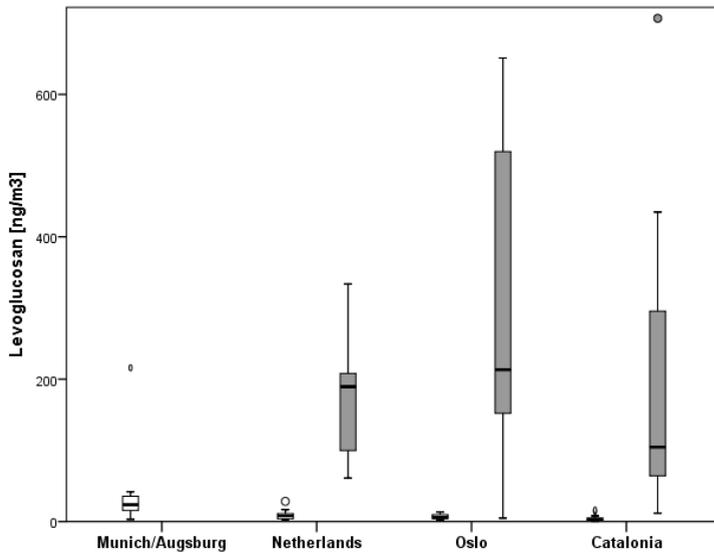


Figure S2. Seasonal differences of levoglucosan. White box – summer, grey box – winter

Table S5. Temporal correlation of levoglucosan with other components (median)

Study area	PM2.5	PM2.5abs	NOX	EC	OC	ΣPAH	B[a]P	Σhopanes/ steranes	K
Oslo	0.931	0.984	0.997	0.999	0.927	0.999	0.998	0.963	0.909
Netherlands	0.674	0.913	0.916	0.920	0.611	0.930	0.946	0.604	0.796
Munich/Augsburg	0.980	0.662	0.996	0.773	-0.016	0.996	0.997	0.760	0.997
Catalonia	0.482	0.913	0.980	0.878	0.988	0.985	0.989	0.922	0.622

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Table S6. Median concentration ratios

Study area	Levo/ PM2.5	Levo/OC	levo/EC	levo/PAH	levo/K	K/levo	
Oslo	0.009	0.056	0.086	71.094	0.931	1.074	Based on annual averages
Netherlands	0.004	0.039	0.048	52.885	0.575	1.739	
Munich/Augsbur g	0.007	0.040	0.075	77.663	0.377	2.653	
Catalonia	0.003	0.017	0.019	36.963	0.247	4.043	
Oslo	0.004	0.027	0.046	66.032	0.335	2.989	All individual measurements
Netherlands	0.004	0.040	0.057	53.379	0.683	1.463	
Munich/Augsbur g	0.004	0.031	0.057	78.210	0.502	1.993	
Catalonia	0.002	0.011	0.013	23.074	0.108	9.236	
Oslo	0.027	0.153	0.173	72.397	2.832	0.353	Cold season
Netherlands	0.006	0.066	0.082	53.379	0.929	1.077	
Munich/Augsbur g	0.011	0.108	0.137	78.118	1.186	0.843	
Catalonia	0.004	0.024	0.028	46.171	0.363	2.754	
Oslo	0.002	0.013	0.020	60.799	0.235	4.260	Warm season
Netherlands	0.001	0.014	0.024	46.054	0.221	4.517	
Munich/Augsbur g	0.003	0.018	0.038	82.535	0.375	2.668	
Catalonia	0.0004	0.003	0.003	7.644	0.034	29.532	

Spatial variations and development of land use regression models of oxidative potential in ten European study areas

Aleksandra Jedynska
Aileen Yang
Menno Keuken
Giulia Cesaroni
Kees de Hoogh
Helgah Makarem Akhlaghi
Konstantina Dimakopoulou
Kees Meliefste
Ole Raaschou-Nielsen
Ingeborg M. Kooter

Gerard Hoek
Marloes Eeftens
Christophe Ampe
Francesco Forastiere
Audrey De Nazelle
Christophe Declercq
Kirsten T. Eriksen
Mark Nieuwenhuijsen
Nicole A.H. Janssen

Meng Wang
Josef Cyrus
Rob Beelen
Marta Cirach
Wenche Nystad
Morgane Stempfelet
Timo Lanki
Tarja Yli-Tuomi
Bert Brunekreef

Abstract

Oxidative potential (OP) has been suggested as a health-relevant measure of air pollution. Little information is available about OP spatial variation and the possibility to model its spatial variability. Our aim was to measure the spatial variation of OP within and between 10 European study areas. The second aim was to develop land use regression (LUR) models to explain the measured spatial variation.

OP was determined with the dithiothreitol (DTT) assay in ten European study areas. DTT of PM_{2.5} was measured at 16-40 sites per study area, divided over street, urban and regional background sites. Three two-week samples were taken per site in a one-year period in three different seasons. We developed study-area specific LUR models and a LUR model for all study areas combined to explain the spatial variation of OP.

Significant contrasts between study areas in OP were found. OP DTT levels were highest in southern Europe. DTT levels at street sites were on average 1.10 times higher than at urban background locations.

In 5 of the 10 study areas LUR models could be developed with a median R^2 of 33%. A European model explained 30% of the measured spatial variability. Overall, LUR models did not explain spatial variation well, possibly due to low levels of OP DTT and a lack of specific predictor variables.

Introduction

Exposure to air pollution has been associated with morbidity and mortality (Brunekreef, Holgate 2002, Pope, Dockery 2006) Epidemiological studies have used mostly the mass of particle matter (PM) with diameters smaller than 10 or 2.5 μm (PM₁₀, PM_{2.5}, respectively) for assessment of exposure to air pollution. The composition and size distribution of PM differs substantially in space and time. There is increasing evidence that the magnitude of adverse health effects depends on PM chemical composition and size distribution (Stanek et al. 2011, Kelly, Fussell 2012). Oxidative potential (OP) has been suggested as a health relevant parameter for epidemiological studies (Borm et al. 2007).

Oxidative potential is defined as a measure of the capacity of PM to oxidize target molecules. Because OP integrates various PM characteristics (e.g. size, chemical composition, biological properties, surface) it might be a more health relevant PM metric than PM mass or single PM compounds (Boogaard et al. 2012, Borm et al. 2007). However, few epidemiological studies have evaluated whether OP of PM predicts health effects better than PM mass. Little is known about the spatial variation of oxidative potential, which is needed to assess whether OP of PM predicts health effects related to long-term exposure better than PM_{2.5} or constituents of PM_{2.5}. Previous studies have documented variability of OP measured with various assays within metropolitan areas (US studies) (Vedal et al. 2013, Hu et al. 2008, Landreman et al. 2008) or single countries (Yang et al. 2014, Yang et al. 2015, Boogaard et al. 2012). Only one study has evaluated spatial contrast between European cities, based upon 20 urban background sites (Kunzli et al. 2006). The authors found significant spatial contrast in the OP levels measured as the ability of PM to generate $\cdot\text{OH}$ in the presence of hydrogen peroxide.

Several chemical assays exist to assess the oxidative potential of PM. They differ from each other in sensitivity to the reactive oxygen species (ROS) generating compounds and analytical method (Ayres et al. 2008). One commonly used assay is based on the consumption of dithiothreitol (DTT) related to the ability of redox active compounds to transfer electrons from DTT to oxygen (Cho et al. 2005, Kumagai et al. 2002). The DTT assay is especially sensitive to organic components such as quinones.

Land use regression models (LUR) have been used increasingly to model the spatial variation of the long term average concentration of the PM_{2.5}, PM₁₀ and the traffic-related pollutants NO₂ and Black carbon (Beelen et al. 2013, Eeftens et al. 2012a). (Hoek et al. 2008). To our knowledge only two studies reported LUR models for oxidative potential (Yanosky et al. 2012, Yang et al. 2015). Yanosky et al. (2012) modeled OP of PM₁₀ in London, where OP was measured as the

depletion rate of antioxidant reduced glutathione (OP^{GSH}). The authors presented a geostatistical spatiotemporal model with an R^2 of 0.52 with two predictors of OP^{GSH} spatial variation: brake and tire wear emissions of PM₁₀ from local traffic with a positive slope and NO_x from heavy-duty vehicles with a negative slope (Yanosky et al. 2012). Yang et al (2015) presented LUR models for 40 Dutch sites for two different OP metrics: DTT and ESR. Both models explained a large fraction of the variation in measured average OP: $R^2 = 0.67$ for OP ESR and $R^2 = 0.60$ for OP DTT. Both models included measured regional background level of OP and traffic related predictors (Yang et al. 2015).

The first aim of this study was to determine the spatial contrast of oxidative potential within and between 10 European study areas. The second aim was the development and evaluation of LUR models of oxidative potential.

In ten European study areas we measured oxidative potential with the DTT assay. 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) (Cyrus et al. 2012, Tsai et al. 2015, Eeftens et al. 2012b). In the framework of these projects concentrations of the pollutants NO_x, NO₂, PM_{2.5}, PM₁₀, PM_{2.5} absorbance and elemental composition were measured in 20 study areas. Measured concentrations and LUR models for these pollutants have been published (Beelen et al. 2013, Eeftens et al. 2012a, Cyrus et al. 2012, de Hoogh et al. 2013, Tsai et al. 2015). In 10 study areas additional characterization of PM was performed, including elemental and organic carbon (EC, OC) and polycyclic aromatic hydrocarbons (PAH) (Jedynska et al. 2014b), levoglucosan (Jedynska, 2015) and oxidative potential.

Methods

Sampling campaign

The ESCAPE sampling campaign has been described in detail previously (Cyrus et al. 2012, Eeftens et al. 2012b). In 10 of the ESCAPE study areas (Table 1), oxidative potential was determined with the DTT assay. All study areas included regional and urban background and major street sites.

Three 14-day integrated samples were collected for each site in a one year period. In four study areas sampling was conducted in 2009, in the other six in 2010. Samples were collected during three seasons: winter, summer and intermediate season (spring or autumn). Due to lack of sampling equipment in Munich/Augsburg, no samples were taken from December to February. Sampling of PM_{2.5} was performed with the Harvard impactor (Eeftens et al. 2012b). For the OP analysis a quartz filter (QMA, Whatman) was used. We used quartz filters for oxidative potential measurements as these were the only filters available for us to

use for OP determination. In a recent comparison study, OP DTT levels on quartz filters were about 20% lower than on Teflon filters. Temporal correlation between DTT on both filter types was high ($R=0.81$) (Yang et al. 2014). The partners in all study areas used identical sampling protocols and criteria for the selection of sampling sites (Eeftens et al. 2012b).

Table 1. Description of study areas. RB –regional background, UB – urban background, S – street location

Country	Study area	Sampling period	Sites	Site types		
				RB	UB	S
Norway	Oslo	05.02.2009 – 29.01.2010	19	2	9	8
Finland	Helsinki/Turku	27.01.2010 – 26.01.2011	20	2	10	8
Denmark	Copenhagen	19.11.2009 – 17.11.2010	20	3	6	11
United Kingdom	London/Oxford	26.01.2010 – 18.01.2011	20	1	12	7
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
France	Paris	04.01.2010 – 04.01.2011	20	4	9	7
Italy	Rome	27.01.2010 – 26.01.2011	20	2	8	10
Spain	Catalonia (Barcelona, Girona, Sabadell)	14.01.2009 – 14.01.2010	40	4	13	23
Greece	Athens	21.04.2010 – 27.04.2011	20	1	12	7

Analytical methods

Filter extraction for oxidative potential measurements

All OP measurements took place in one laboratory (TNO). 2.4 cm² of each quartz filter (30% of the filter) was extracted in 20 ml ethanol for 1 hour in an ultrasonic bath. Further, the extracts were filtered with 0.45 µm PTFE syringe filters to remove quartz particles and dried under constant flow of nitrogen. At the end extracts were reconstituted in 100 µl ethanol and 900 µl MiliQ water.

DTT assay

The DTT assay measures the presence of reactive oxygen species via formation of DTT-disulfide due to transfer of electrons from DTT to ROS by recycling chemicals such as quinones (Cho et al. 2005).

In brief, aliquots of extracts were incubated with DTT (Sigma, Zwijndrecht). The reaction was stopped at designated time points (0, 10, 20, 30, 40 and 50 min), adding 5,50-Dithiobis(2-nitrobenzoic acid) (DTNB) (Sigma).

The absorption at 412 nm is measured, and the rates are calculated using linear regression of absorbance against time. The results are expressed as nmol DTT/min*m³. A soot sample obtained from exhaust pipe of city busses was used as a positive control and ultrapure water as a negative control.

Quality control

To maximize comparability of the sampling in different countries, sampling and measurement procedures were conducted according to standard protocols. All OP analyses were performed centrally in the TNO lab in the Netherlands. We did not have enough equipment available to include field blanks and duplicates for OP analyses. OP methods used at TNO have been validated according to the Dutch national norm (NEN-7777, 2003 <https://www.nen.nl/NEN-Shop/Norm/NEN-7777C12012-en.htm>). The following checks were performed in the laboratory: Milli-Q blanks, quality control samples – soot sample as a positive control for OP DTT assay.

EC/OC, PAH, hopanes, steranes, levoglucosan, PM_{2.5}, NO_x and elemental composition

The analytical methods of EC/OC, PAH, hopanes/steranes, levoglucosan, PM_{2.5}, NO₂ and elemental composition were published previously (Jedynska et al. 2014b) and are summarized in the Online supplement.

Adjustment for temporal variability

The three 14-day average - samples were used to calculate the annual average level of oxidative potential. As we could not collect samples simultaneously at all sites, the simple average from the concentrations in the three sampling periods could reflect both spatial and temporal variation. In order to correct for temporal variation, a (background) reference site was continuously measured in each study area during the sampling period. Our correction procedure followed the modified ESCAPE procedure used for EC/ OC, PAH, hopanes/steranes and levoglucosan (Eeftens et al. 2012b, Cyrus et al. 2012, Jedynska et al. 2014b, Jedynska et al. 2015). Briefly, we evaluated which of the pollutants measured at the reference site, correlated best with OP. The temporal correlation was calculated for each site between OP and the main ESCAPE pollutants NO_x, NO₂, PM_{2.5}, PM_{2.5} absorbance and PM₁₀ based upon three samples. The median correlation per study area was calculated and the pollutant with the highest median correlation with OP was used for correction of temporal variation, using the ratio method as we did for EC/OC, PAH, hopanes/steranes and levoglucosan (Jedynska et al. 2014b).

Predictor data for LUR model development

Derivation of predictor variables has been presented in detail (Eeftens et al. 2012a, Beelen et al. 2013). Briefly, the predictor variables mainly describe potential emission sources such as traffic, industry or residential emissions. The predictor variables were determined for each sampling site using a geographical information system (GIS). Most variables were circular buffers around the sampling site. A detailed description of the variables is presented in online supplement Table S1.

LUR model development

LUR models were developed by the first author using the ESCAPE method (Beelen et al. 2013, Eeftens et al. 2012a, de Hoogh et al. 2013). Briefly, adjusted annual average concentration of oxidative potential 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 traffic intensity predicts higher OP. The final model was 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).

Models were developed for each of the 10 study areas separately and for the combined dataset. Wang et al (2014) recently documented the feasibility of developing European models combining all ESCAPE study areas for PM_{2.5}, PM_{2.5} absorbance and NO₂ (Wang et al. 2014). We developed European models with indicators for study area and another model with the measured regional OP background in each study area as a predictor variable. The latter approach is comparable to the multi-city model for PM_{2.5}, PM_{2.5} absorbance and NO₂ (Wang et al. 2014).

Data analysis

All measurements' results were analyzed centrally at TNO. Statistical analyses were performed with the SPSS statistical program (IBM SPSS Statistics 20).

We assessed the significance of differences of adjusted annual OP averages between study area with analysis of variance (ANOVA). Student's t-tests were used to evaluate the difference between site types and between seasons. We analyzed seasonal differences based on all individual measurements divided into the warm (April – September) and cold period (October – March).

Results and discussion

The detection limit (LOD) of DTT, calculated as three times the standard deviation of laboratory blanks, was 0.078 nmolDTT/min*m³. 15% of all samples gave results below the LOD. The uncertainty of the DTT assay is 24%. Calculation of uncertainty (Uc) was based on: reproducibility (vc), recovery (utv) and accuracy of the calibration standard (uj) according to the following formula: $(Uc = \sqrt{((vc)^2 + (uj)^2 + (utv)^2})}$.

Temporal adjustment

The main focus is on adjusted annual average concentrations. In five study areas OP DTT was corrected for temporal variation with PM_{2.5}, in four with NO_x and in one with PM_{2.5} absorbance. The high correlation ($R > 0.90$ in all areas except Helsinki, where R was 0.60) between the selected pollutant and OP at the sampling sites documents that the temporal variation of OP was well reflected by these pollutants. Adjusted and unadjusted annual OP averages were mostly highly correlated. Pearson correlation coefficients were between 0.65 and 0.98 (Table S2). This documents that the adjustment did not change the results much.

Within and between study area contrast

The spatial variation within and between study areas is presented in Figure 1 and Table 2. Levels of OP DTT across Europe differed significantly (Figure 1, Table 2). The lowest OP DTT level were found in London (0.14 nmolDTT/min * m³) and two Nordic areas – Oslo and Helsinki/Turku (0.13 and 0.15 nmolDTT/min * m³, respectively).

OP DTT levels were highest in southern study areas, but the differences between the three southern and the three northern study areas were smaller (south/north ratio = 1.5) than we found for traffic-related pollutants including NO₂, and EC (south/north ratio – 2.2) and for PM_{2.5} mass (south/north ratio – 2.1), (Eeftens et al. 2012b, Cyrus et al. 2012, Jedynska et al. 2014b).

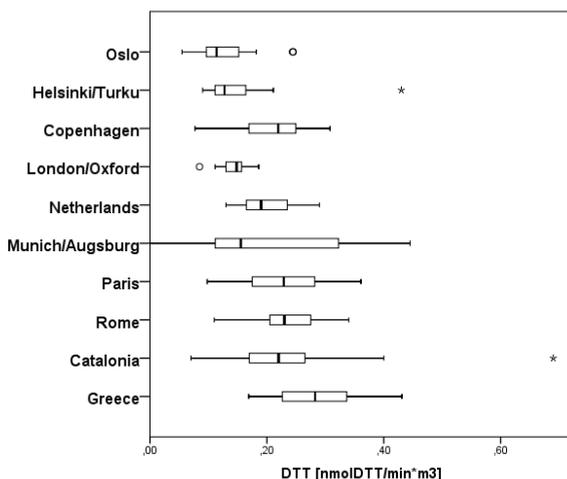


Figure 1. Distribution of OP DTT (nmolDTT/min * m³) in different study areas. Median, 25th and 75th percentiles are shown in the box, whiskers indicate 10th and 90th percentiles and individual outliers are shown.

Table 2. Mean and range of annual average oxidative potential for 10 European study areas

Study area	n	DTT (nmolDTT/min * m ³)			
		Mean	Min	Max	Range/Mean [%]
Oslo	19	0.13	0.06	0.25	149
Helsinki/Turku	20	0.15	0.09	0.43	229
Copenhagen	20	0.21	0.08	0.31	109
London/Oxford	20	0.14	0.08	0.19	71
Netherlands	16	0.20	0.13	0.29	80
Munich/Augsburg	20	0.20	0.00	0.45	221
Paris	20	0.23	0.10	0.36	115
Catalonia	40	0.23	0.07	0.69	271
Rome	20	0.23	0.11	0.34	98
Athens	20	0.28	0.17	0.43	92

Note: differences between study areas statistically significant (ANOVA, $p < 0.0001$)

Table 3. Difference of annual average oxidative potential levels between site types (ratios RB/UB and S/UB)

Study area	DTT (nmolDTT/min*m ³)	
	RB/UB	S/UB
Oslo	0.82	0.88
Helsinki/Turku	0.85	0.71
Copenhagen	1.22	1.05
London/Oxford	1.12	1.06
Netherlands	0.90	1.14
Munich/Augsburg	1.73	1.11
Paris	0.95	1.15
Rome	1.63	1.12
Catalonia	0.99	1.10
Athens	0.63	1.21
Median	0.97	1.10

The smaller contrast across Europe is consistent with the small difference between street and urban background locations found in this study (Table 3). In 8 of the 10 study areas, concentrations at the street sites were slightly higher than at the urban background sites with a median S/UB ratio of 1.10. Our findings are in line with a few previous studies which also reported low contrast of OP DTT between street and background sites. In a recent study based upon extraction of the Teflon PM_{2.5} filters of all 40 ESCAPE sites in the Netherlands/Belgium, the street locations had 1.2 times higher OP DTT than urban background sites (Yang et al. 2015). In our study, the Dutch S/UB ratio, based on 16 of these 40 sites, was very similar – 1.14.

In another Dutch study with five sites, OP DTT was 1.2 times at a busy urban street site than at urban background (Janssen et al. 2014). The ratio between a highway site to an urban background site was higher (ratio 2.1). In our study we did not have street sites with as heavy traffic as on highways.

In a study investigating OP in the Los Angeles harbor area, a modest contrast in DTT results between different sites was found (Hu et al. 2008). The ratio between traffic and background sites was on average 1.3.

Our study conducted in 10 different European study areas supports a growing literature that OP DTT does not reflect large urban traffic contrasts (Yang et al. 2015, Janssen et al. 2014, Hu et al. 2008). The assay may respond to components from non-traffic sources resulting in a high background.

The OP DTT S/UB ratio found in our study was lower than for other pollutants measured at the same sites including NO₂, EC, PAH and OC (Eeftens et al. 2012b, Cyrus et al. 2012, Jedynska et al. 2014b). As the DTT assay responds primarily to organic compounds, particularly the substantially lower contrast compared to OC (median S/UB = 1.32) and PAH (median S/UB = 1.44) is remarkable. We did not measure quinones, components which are thought to especially affect the DTT assay. Quinones are oxygenated aromatic compounds e.g. oxy-PAH, emitted during incomplete combustion processes including traffic (Jedynska et al. 2015b).

There was no consistent difference between urban and regional background sites (median RB/UB = 0.97). In four study areas (London/Oxford, Munich/Augsburg, Copenhagen, Rome), OP DTT was higher at the regional sites. In three of these areas (London, Munich/Augsburg, Rome) OC concentrations were also increased at the regional sites (Jedynska et al. 2014b). This suggests that sources of organic components that affect OP DTT may be present in more rural areas. At the regional background sites, Yang et al found lower OP DTT level than at the urban background sites (ratio 0.8), consistent with our results for the Netherlands (0.9).

The mean OP DTT levels were only 2-4 times higher than the LOD (Table 2). OP DTT levels were also low compared to levels found in other studies (Saffari et al. 2014, Janssen et al. 2014, Yang et al. 2014). The low OP DTT concentrations were related to the use of quartz filters (Yang et al. 2014). We furthermore only extracted a section of the filter, as we also determined EC/OC and levoglucosan on the same filter. Quartz filters for PM collection in order to determine oxidative potential are not very common. In most studies PM was collected in a solution with the Versatile Aerosol Concentrator Enrichment System (VACES) (Cho et al. 2005, Ntziachristos et al. 2007) or Teflon filters were used (Janssen et al. 2014, Kunzli et al. 2006). We found one study where quartz filters were used for OP DTT measurements (Vedal et al. 2013). Yang et al. reported significantly lower OP levels for samples taken on quartz filters than on Teflon filters for four different OP assays, including DTT, with

20% lower results than samples taken on Teflon filters (Yang et al. 2014). The correlation between measurements on quartz and Teflon was high ($R=0.8$). The correlation was based on 15 measurements taken at two sites. For the Dutch data, a direct comparison with OP DTT measured on ESCAPE Teflon filters was available from another study (Yang et al. 2015). The correlation for the 16 sites was moderate for the unadjusted average concentration ($R^2=0.26$) and low for adjusted average concentration ($R^2=0.12$) (Figure S1).

Compared to the previous comparison study (Yang et al. 2014), the differences in absolute levels between Quartz and Teflon OP DTT were much larger. OP DTT levels on quartz in the previous comparison were 20% lower and highly correlated ($R^2=0.66$) with Teflon OP DTT (Yang et al, 2014). In the previous comparison all samples were analyzed in one laboratory, whereas in the current comparison samples were analyzed in different labs. The comparison of DTT analyses between the two laboratories revealed substantial differences in DTT levels with much lower TNO results, (Figure S2) (TNO report TNO-060-UTP-2013-00038). OP assays have not yet been standardized sufficiently to allow comparison of the results obtained at different laboratories.

Land use regression modelling

Individual study areas

For five out of ten study areas a LUR model could be developed (Table 4). The median R^2 for the 5 models was 33%. The lowest R^2 was found in Catalonia ($R^2 = 0.13$) and the highest in The Netherlands and Oslo (0.73 and 0.66 respectively). In those two study areas the LOOCV R^2 was higher than 50%. No traffic related variables were included in the models. In three study areas variables describing population density were included. In two study areas variables related to green space were included. In four models only one significant predictor variable was identified. In Paris only altitude was included in the model.

DTT model predictions were moderately correlated with both PM2.5 model prediction (median $R=0.33$) and with PM2.5 absorbance (median $R=0.36$) (Table 4).

In four of the five areas where no model was possible, the regional background OP measurements were higher than the urban background (Table 3). Our procedures did not allow a negative slope for address or population density, predictors with lower values at regional background sites. When an indicator variable for urban (0/1) was included and a negative slope allowed, models could be developed for Rome, Munich/Augsburg, London/Oxford and Helsinki/Turku with model R^2 of 17 to 52%. The rationale for this sensitivity analysis is that we are less certain about source impacts on OP DTT than on pollutants such as NO_2 and PM2.5 for which the procedures were developed. The Rome model included the indicator variable urban and distance to a major road ($R^2=52\%$). The Munich/Augsburg model

included the urban indicator variable and traffic load in a 100m buffer ($R^2=30\%$). The London model included the urban indicator variable and major road length in a 100m buffer ($R^2=17\%$). In Helsinki/Turku, a model was only possible including residential density in a 50m buffer if a high Cooks D was allowed ($R^2=17\%$).

European model

A European level model combining all ten study areas resulted in a model R^2 of 30%, with port and small scale residential density in addition to indicator variables for study areas (Table 4). A model with indicator variables alone explained 25% of the variability.

When we used measured regional background to characterize the study area, instead of indicator variables, a model was developed with four predictor variables that explained 24% of the variability in OP DTT. The developed model was: $0.0889+6.09E-09*PORT_5000+6.44E-11*Traffic_load_1000+0.379*Regional\ Background+1.34E-6*Population_500$. In this model more of the variability was explained by GIS predictors (regional background OP DTT alone explained 5.3%).

Overall, land use regression models did not explain spatial variation of OP DTT well. LUR models could be developed only for five out of ten study areas. The explained variance of the developed OP LUR models was low (median $R^2 = 33\%$) in comparison to frequently modeled pollutants like PM_{2.5} or pollutants used as traffic markers – NO₂ or PM_{2.5} absorbance for which model R^2 higher than 70% were found in ESCAPE (Beelen et al. 2013, Eeftens et al. 2012a). The European level model combining all ten study areas resulted in a low model R^2 as well, but the gap between model and leave-one out cross validation R^2 was much smaller than for the individual area models. The smaller gap is due to the larger number of monitoring sites to train the model (Wang et al. 2012). The European model contained more predictor variables (port, population density) than the study-area specific models (e.g. altitude and large scale natural land in Paris and Athens). Recently, several European and American studies reported large-scale LUR models for PM, NO₂ and soot (Novotny et al. 2011, Wang et al. 2014, Vienneau et al. 2013). Large-scale LUR models can provide improved prediction of pollutant concentrations for study areas with poor or no local models.

We found only two published study reporting a LUR for oxidative potential (Yanosky et al. 2012, Yang et al. 2015). In London, models were based on weekly averages of OP of PM₁₀ measured with antioxidant reduced glutathione (GSH) at 66 sites. The explained variance of the developed model was 50%. The variables used were: PM₁₀ brake and tire wear, emissions from all vehicles within 50m and NO_x tailpipe emissions from heavy-goods vehicles within 100m. In our study we could not develop a LUR DTT model for London/Oxford study area, related to

Table 4. Description of LUR models for OP DTT (nmolDTT/min * m³)

Study area	LUR model	n	R ² [%]	LOOCV R ² [%]	RMSE	R ² with PM2.5 [#]	R ² with PM2.5abs [#]
Oslo	$0.0547 + 0.000181 \times \text{HHOLD_300}$	19	66	59	0.031	0.27*	0.14
Helsinki/Turku	NM						
Copenhagen	NM						
London/Oxford	NM						
Netherlands	$0.193 + 0.0000149 \times \text{POP_300} - 0.00000104 \times \text{UGNL_300} - 2.376 \times 10^{-9} \times \text{NATURAL_5000}$	16	73	50	0.028	0.26*	0.25*
Munich/Augsburg	NM						
Paris	$0.367 - 0.0164 \times \text{SQRALT}$	20	25	5	0.063	0.33**	0.38**
Rome	NM						
Catalonia	$1.268 + 0.00000641 \times \text{HDRES_500}$	39	12	6	0.070	0.30**	0.36**
Athens	$0.324 - 5.045 \times 10^{-9} \times \text{NATURAL_5000}$	20	33	22	0.064	0.49**	0.29*
Median			33	22			
Combined 10 area model with indicators for area	$0.188 - 0.10001 \times \text{land1} - 0.06504 \times \text{land2} - 0.03328 \times \text{land3} - 0.08856 \times \text{land4} - 0.05127 \times \text{land5} + 0.00893 \times \text{land6} - 0.02609 \times \text{land7} + 0.05424 \times \text{land8} + 0.00384 \times \text{land9} + 6.82\text{E-}04 \times \text{PORT_5000} + 0.00000139 \times \text{HDLRES_100}$	215	30	26	0.768		

Description of variables used in the models: NATURAL Semi-natural and forested areas, UGNL Combined urban green and natural land, HDRES High density residential land, SQRALT Squared altitude, HHOLD number of households, POP number of inhabitants, NM = no model possible. R with PM2.5 is the correlation of the OP model prediction with the predictions of previously published PM2.5 models at sites not used for modelling.

Correlation between LUR model predictions of OP DTT and PM2.5 and PM2.5abs. ** p value < 0.01, * p value < 0.05

Study area indicators compared to Catalonia as the reference (n=40 sites). Land1 – Oslo, land2 – Helsinki/Turku, land3 – Copenhagen, land4 – London/Oxford, land5 – Netherlands, land6 – Munich/Augsburg, land7 – Paris, land8 – Rome, land9 – Athens.

either a different assay, the very low within study area contrast or a smaller number of locations than in the Yanosky study.

A recent Dutch study reported LUR models for two OP assays: DTT and ESR developed for the 40 Dutch ESCAPE sites. Reported R^2 of OP DTT LUR model was lower (60%) than the R^2 in our study for the Netherlands (73%). Both models differed in included variables. Our models included population density variable and variables describing natural areas while Yang et al developed a model containing regional OP DTT level, traffic related variables and natural area variable. The differences between two Dutch models might be caused by different number of used sites used for model development, different OP DTT levels (discussed before), and included regional OP DTT levels in the model.

Performance of OP DTT models

The relatively poor general performance of LUR models for OP DTT is likely due to a combination of: 1. The low measured levels of OP DTT relative to the LOD; 2. The lack of specific GIS predictor variables for OP DTT and 3. Insufficient understanding of sources related to urban – rural differences of OP.

First, due to the use of quartz filters, measured OP values did not exceed the LOD much and therefore the measurement error may have been relatively large. This is supported by the low to moderate correlation between our OP DTT measurements and OP DTT measurements on Teflon filters previously reported for the Dutch sites. Random error in a dependent variable in linear regression analysis does not lead to bias of the regression slopes of the model, but does lead to a loss in precision (Armstrong 1998). This implies that the correct LUR model may be identified but with low model R^2 . This theory may apply more for the European model based upon a large number of sites than for individual area models. Similar observations of a robust spatial model with a low model R^2 have recently been made in a LUR study based upon mobile monitoring (Montagne et al. 2015). Mobile monitoring also resulted in large random error per site. Second, relatively low explained variance of LUR models for DTT might further be caused by the lack of variables describing oxidative potential sources other than traffic e.g. wood burning, specific industries or agricultural activities. Recently published, land use regression models developed for components with other sources than traffic also had substantially lower explained variance than components with traffic markers (de Hoogh et al. 2013, Jedynska et al. 2015a).

LUR models for elemental composition of PM_{2.5} 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 (50-60%), still substantially higher than found in this study for OP. A moderate explained variance was also reported for wood smoke marker levoglucosan in a subset of four of our study areas (Oslo, Netherlands, Munich, Catalonia) (Jedynska et al. 2015a).

Recently, we also found moderate explained variance for LUR models for PAH and OC (median $R^2 = 59\%$ and 65% , respectively), probably due to the contribution of less well characterized sources of those pollutants (Jedynska et al. 2014a).

Third, the observation that models could not be developed with our procedures especially in areas with higher regional background than urban background, suggests that we may not fully understand sources contributing to measured OP DTT. The rationale for specifying a fixed direction of slope for predictor variables is to avoid implausible models (Wang et al. 2012).

Seasonal differences

Comparison of all measurements in two periods (cold and warm) showed higher concentrations during the cold period in 9 out of 10 study areas (Table S3). Helsinki/Turku had slightly higher concentrations in the warm period. The median cold/warm ratio was 1.51. The higher concentrations of air pollutants in the cold period are mainly caused by higher pollutant emissions (heating) and poorer dispersion because of less vertical mixing during the warm period.

The OP DTT cold to warm ratio of 1.51 was lower than the ratio found for levoglucosan (6.3), a marker of wood combustion, with known high seasonality and Σ PAH (4.5), which are also influenced by more intensive domestic heating during winter (Jedynska et al. 2014b).

The OP DTT cold to warm ratio was similar as the ratio for OC, which has various primary and secondary sources (1.9), and EC, used as traffic marker (1.3).

For air pollutants with traffic as a dominant source, emissions do not differ much between winter and summer and the higher concentration ratios are largely due to poorer dispersion conditions. Our cold/warm increases suggest that emission of components to which the DTT assay responds were fairly constant across seasons as well. There are few studies comparing OP levels between seasons. In an American study DTT levels between seasons in several locations differed less than in our study (winter/summer ratio = 1.2) (Vedal et al. 2013). In our study we used similar extraction method and we used also quartz filters for the sampling which makes comparison of the results easier.

Conclusions

Significant spatial contrasts were found for OP DTT between 10 European study areas. The OP DTT levels were the highest in southern and the lowest in northern Europe. Our study conducted in 10 different European study areas supports a growing literature that OP DTT does not reflect large urban traffic contrasts. At street sites slightly higher OP DTT values were found than at urban background sites (median ratio 1.10). For five out of ten study areas LUR models could be

developed for OP DTT with a relatively low explained variance (median $R^2 = 33\%$). Overall, land use regression models did not effectively explain spatial variation of OP DTT possibly due to low levels of OP DTT and a lack of specific predictor variables. A European level model combining all ten study areas resulted in a model with more specific predictor variables than the study-area specific models.

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Chapter 5

Appendix

Measurement of EC/OC, PAH, hopanes, steranes, levoglucosan, PM_{2.5}, NO_x and elemental composition

The analytical methods of EC/OC, PAH and hopanes/steranes were published previously (Jedynska, Hoek et al. 2014c). In summary, 1cm² of each quartz filter was used for EC/OC analyses, using a thermal-optical analyzer (Sunset Laboratory, Inc., Oregon, USA).

T60A20 filters were used for measurements of 16 EPA PAH and 13 hopanes/steranes via gas chromatography in combination with mass spectrometric detection (GC/MS) in electron impact mode (GC/MS EI, Agilent 6890/5973N).

The analytical method for levoglucosan is described elsewhere (Jedynska, Hoek et al. 2014a). Levoglucosan was measured with gas chromatography in combination with mass spectrometric detection (Agilent 6890/5973N GC/MS).

PM_{2.5} mass and absorbance were determined on Andersen 37 mm 2 µm pore size Teflon filters (Eeftens, Tsai et al. 2012). Reflectance of all filters was measured in IRAS laboratory and transformed into absorbance. NO₂ was measured with Ogawa passive samplers (Cyrus, Eeftens et al. 2012).

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

Table S1. Predictor variables with predefined variable names, units, defined buffer sizes, transformations of the predictor variables and directions of effect.

GIS dataset	Predictor variable	Name variable ¹	Unit	Buffer size (radius in m)	Direction of effect	Central / local data
Background variables						
CORINE	Surface area of high density residential land	HDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of low density residential land	LDRES_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Sum of high density and low density residential land	HLDRS_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of industry	INDUSTRY_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of port	PORT_X	m ²	100, 300, 500, 1000, 5000	+	Central
CORINE	Surface area of urban green ²	URBGREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Surface area of semi-natural and forested areas ³	NATURAL_X	m ²	100, 300, 500, 1000, 5000	-	Central
CORINE	Sum of Urban green and Semi-natural and forested areas	GREEN_X	m ²	100, 300, 500, 1000, 5000	-	Central
Local land use	Similar to CORINE variables	Similar to CORINE variables	m ²	100, 300, 500, 1000, 5000	As CORINE	Local
Local land use	Surface area / number of buildings	BUILDINGS_X	m ² / N(number)	100, 300, 500, 1000, 5000	+	Local
Local land use	Surface area of water	WATER_X	m ²	100, 300, 500, 1000, 5000	-	Local
Population density	Number of inhabitants	POP_X	N(number)	100, 300, 500, 1000, 5000	+	Central / Local
Household density	Number of households	HHOLD_X	N(number)	100, 300, 500, 1000, 5000	+	Local
Altitude	Altitude	SQRALT	m	NA	-	Local
-	Regional estimate ⁴	REGIONALESTIMATE	NA	NA	NA	Local
-	Coordinate variables ⁴	XCOORD, YCOORD or other combinations	m	NA	NA	Local
Traffic variables						
Central road network	Road length of all roads in a buffer	ROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central
Central road network	Road length of major roads in a buffer ⁵	MAJORROADLENGTH_X	m	25, 50, 100, 300, 500, 1000	+	Central
Central road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEARC1 DISTINVNEARC2	m ⁻¹ , m ⁻²	NA	+	Central

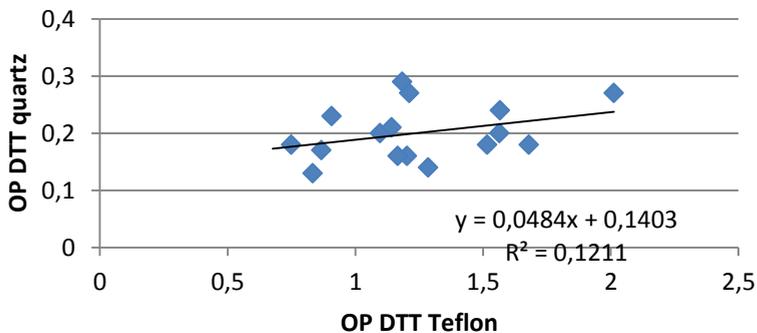
Central road network	Inverse distance and inverse squared distance to the nearest major road ⁵	DISTINVMAJORC1	m ⁻¹ , m ⁻²	NA	+	Central
Local road network	Traffic intensity on nearest road	DISTINVMAJORC2 TRAFNEAR	Veh.day ⁻¹	NA	+	Local
Local road network	Inverse distance and inverse squared distance to the nearest road	DISTINVNEAR1 DISTINVNEAR2	m ⁻¹ , m ⁻²	NA	+	Local
Local road network	Product of traffic intensity on nearest road (TRAFNEAR) and inverse distance to nearest road (DISTINVNEAR1) and distance squared (DISTINVNEAR2)	INTINVVDIST INTINVVDIST2	Veh.day ⁻¹ Veh.day ⁻¹ m ⁻²	NA	+	Local
Local road network	Traffic intensity on nearest major road ⁶	TRAFMAJOR	Veh.day ⁻¹	NA	+	Local
Local road network	Inverse distance and inverse squared distance to the nearest major road ⁶	DISTINVMAJOR1 DISTINVMAJOR2	m ⁻¹ , m ⁻²	NA	+	Local
Local road network	Product of traffic intensity on nearest major road (TRAFMAJOR) and inverse of distance to the nearest major road (DISTINVMAJOR1) and distance squared (DISTINVMAJOR2) ⁶	INTMAJORINVDIST INTMAJORINVDIST2	Veh.day ⁻¹ Veh.day ⁻¹ m ⁻²	NA	+	Local
Local road network	Total traffic load of major roads in a buffer (sum of (traffic intensity * length of all segments)) ⁶	TRAFMAJORLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+	Local
Local road network	Total traffic load of all roads in a buffer (sum of (traffic intensity * length of all segments))	TRAFLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+	Local
Local road network	Heavy-duty traffic intensity on nearest road	HEAVYTRAFNEAR*	Veh.day ⁻¹	NA	+	Local
Local road network	Product of heavy-duty traffic intensity on nearest road (HEAVYINT) and inverse of distance to the nearest road (INVDIST) and distance squared (INVDIST2)	HEAVYINTINVDIST HEAVYINTINVDIST2	Veh.day ⁻¹ Veh.day ⁻¹ m ⁻²	NA	+	Local
Local road network	Heavy-duty traffic intensity on nearest major road ⁶	HEAVYTRAFMAJOR	Veh.day ⁻¹	NA	+	Local
Local road network	Total heavy-duty traffic load of major roads in a buffer (sum of (heavy-duty traffic intensity * length of all segments)) ⁶	HEAVYTRAFMAJORL OAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+	Local
Local road network	Total heavy-duty traffic load of all roads in a buffer (sum of (heavy-duty traffic intensity * length of all segments))	HEAVYTRAFLOAD_X	Veh.day ⁻¹ m	25, 50, 100, 300, 500, 1000	+	Local

Chapter 6: General discussion

Table S2: Pearson correlation (r) between unadjusted and ratio-adjusted concentrations of oxidative potential

Study area	DTT
Oslo	0.83
Helsinki/Turku	0.95
Copenhagen	0.86
London/Oxford	0.65
Netherlands	0.88
Munich/Augsburg	0.92
Paris	0.90
Rome	0.93
Catalonia	0.82
Athens	0.98

a)



b)

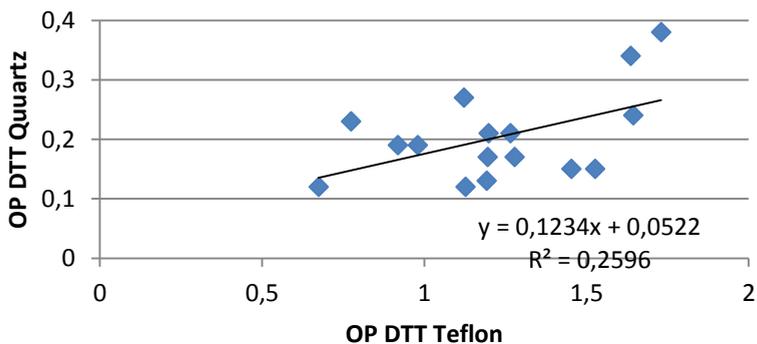


Figure S1. Comparison between OP DTT measurement on quartz filters (this study) and Teflon filters (Yang, 2015). a) Unadjusted average OP, b) Adjusted average OP

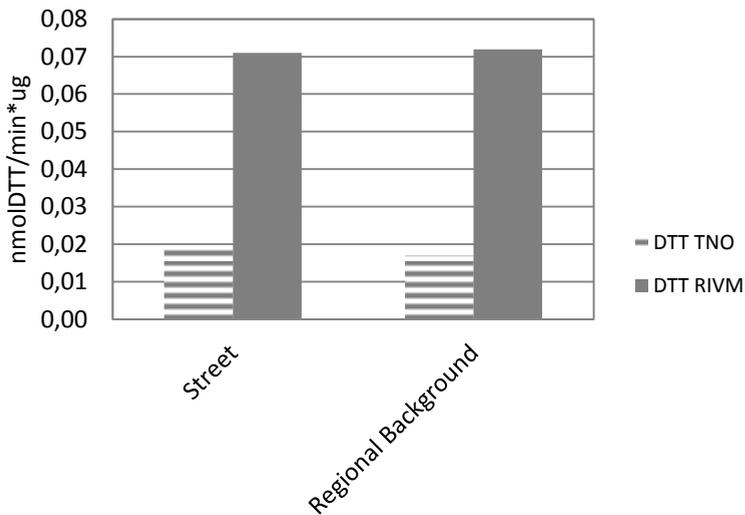


Figure S2. Comparison of DTT results between two laboratories: TNO and RIVM (TNO REPORTI TNO-060-UTP-2013-00038).

Table S3. Difference of OP DTT annual levels between cold and warm periods

Study area	DTT
	Cold/Warm
Oslo	2.60**
Helsinki/Turku	0.88
Copenhagen	1.88**
London/Oxford	1.43**
Netherlands	1.50*
Munich/Augsburg	1.85**
Paris	1.52**
Rome	2.01**
Catalonia	1.35*
Athens	1.45**
Median	1.51

Chapter 6

General discussion

The objectives of this thesis were to determine spatial contrast of specific air pollutants (EC/OC, PAH and hopanes/steranes, levoglucosan and oxidative potential) within and between European study areas and to develop and evaluate LUR models for those components. The research was conducted in the framework of two European Union funded projects: TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) and ESCAPE (European Study of Cohorts for Air Pollution Effects).

Main findings

In **Chapter 2**, the spatial variation of EC/OC, PAH and hopanes/steranes between and within 10 European study areas is presented. We also assessed the spatial relationship between those components and the more frequently measured NO_x , NO_2 , $\text{PM}_{2.5}$ mass and absorbance. Substantial variability was found in spatial patterns of EC, OC, PAH and hopanes/steranes. EC and OC concentrations had similar patterns in Europe as the previously reported components NO_x , $\text{PM}_{2.5}$ and PM absorbance. The highest concentrations for those pollutants were found in southern Europe. The highest average EC and OC concentrations were found in Rome, where levels were 2.3 and 3.7 $\mu\text{g}/\text{m}^3$, respectively. In Oslo, EC and OC concentrations were lowest at 0.8 and 1.1 $\mu\text{g}/\text{m}^3$, respectively. ΣPAH exhibited a different trend in Europe. In southern and northern Europe, concentrations of those pollutants were similar with the highest concentrations in Copenhagen (2.1 ng/m^3), Rome and Athens (both 2.0 ng/m^3). The developed LUR models for those components for each of the ten study areas (four models for hopanes and steranes as these were measured in four areas only) and their evaluation are presented in **Chapter 3**. The highest median of the ten model explained variances (R^2) was found for EC – 84%. The median model R^2 for OC was 51%, for benzo[a]pyrene, 67% and for the sum of hopanes/steranes, 38%. Traffic predictors were included in most models. The correlation of predictions from these PM composition LUR models with predicted $\text{PM}_{2.5}$ and $\text{PM}_{2.5}$ absorbance was on average moderate but varied substantially between study areas. The median correlation between predictions of $\text{PM}_{2.5}$ models and OC and ΣPAH models, was 0.47 and 0.52, respectively.

In **Chapter 4** the spatial variation of the wood smoke marker levoglucosan between and within four study areas (Oslo in Norway, The Netherlands, the Munich/Augsburg region of Germany and Catalonia in Spain) is presented. Levoglucosan concentrations were highest in Munich/Augsburg (102 ng/m^3) and lowest in Catalonia (64 ng/m^3), although the differences were not statistically significant. The contribution of wood-smoke, calculated on the basis of levoglucosan measurements and previous European emission data. to OC and $\text{PM}_{2.5}$ mass was 13 to 28% and 3 to 9% per study area respectively over the full

year studied. Larger contributions were calculated for the cold period. Across all areas, the highest within-study area correlation of levoglucosan was found with Σ PAH and B[a]P with median correlation coefficients of 0.65 and 0.58, respectively. The lowest correlation was found between levoglucosan and traffic markers: Σ hopanes/steranes and NO_x (median $r = -0.22$). A relatively poor correlation was found between potassium in $\text{PM}_{2.5}$ (another marker for wood smoke) and levoglucosan (median $r = 0.33$). Finally, we developed and evaluated LUR models of levoglucosan for the four study areas. All models had a reasonably high R^2 . The lowest R^2 was found in Oslo ($R^2 = 0.59$) and the highest in Catalonia ($R^2 = 0.71$). Variables used in our models were unspecific for wood combustion emissions, but were variables associated with general human activity. Wood smoke emission data available from an emission inventory on a 6x6 km scale did not improve LUR models.

In **Chapter 5** we present the spatial variation of oxidative potential measured with the DTT assay between and within ten European study areas. Significant spatial contrasts were found for OP DTT between the study areas. The lowest OP DTT level were found in London and two Nordic areas – Oslo and Helsinki/Turku (0.14, 0.13 and 0.14 $\text{nmolDTT}/\text{min}\cdot\text{m}^3$ respectively). The highest OP levels were found in southern Europe, but the difference with the Nordic areas was smaller than for $\text{PM}_{2.5}$ and NO_2 . At street sites slightly higher OP DTT values were found compared to urban background sites (median ratio 1.10). LUR models could only be developed for OP DTT for five out of ten study areas. A relatively low explained variance (median $R^2 = 33\%$) was found for the five areas. A European level model combining all ten study areas resulted in a model R^2 of 30%, which was more robust than than the study-area specific models. The model included residential density, port and traffic variables.

My thesis work contributes new insights into characterization of air quality by monitoring and modelling of specific organic components and oxidative potential. I integrate the discussion of my work in two main themes, namely 1) air quality monitoring and 2) modelling of PM composition. For air quality monitoring I will address the question of whether it would be useful to add the components I measured to routine monitoring networks. For modelling, I want to address the success and limitations of PM composition modelling, but also possible improvements of land use regression and dispersion modelling. More specifically, I will address the following topics:

1. Air quality monitoring networks and the merit of monitoring additional pollutants.

I will discuss current European air quality monitoring legislation (section 1.1), design of current air quality monitoring network in Europe and supersites (section

1.2) and then discuss the question: Should European air quality monitoring be expanded? I will try to answer this question by analysing the following aspects of particle components:

- Health effects of PM composition
- Spatial and temporal variation of PM organic pollutants
- Specificity of individual air pollution markers (OC, OP, PAH, levoglucosan) and their correlation with PM mass and elements
- Organic pollutants' monitoring cost and practicability

2. Modelling of concentrations of PM components

I will discuss land use regression models of PM composition (section 2.1), dispersion modelling of PM components (section 2.2) and possible improvements of modelling of specific PM components by LUR and dispersion models (section 2.3).

1. Air quality monitoring networks and the merit of monitoring additional pollutants.

1.1 Current European Air quality monitoring – legislation

The European directives regulating ambient air quality are designed to reduce the adverse effects of air pollutants on human health and the environment by implementing limit or target values for ambient concentrations of air pollutants. They describe the method of the assessment and management of air quality and set concentration limits or target values for a limited number of pollutants for which then monitoring requirements are specified (methods, locations, averaging times etc.). When limits are exceeded, authorities must develop and implement air quality management plans to comply with the European regulations.

For many years the air pollution guidelines have considered all particulate matter (PM) as equally toxic and regulated only PM mass concentration. A growing number of studies suggest that adverse health effects may depend on PM composition and that individual PM components may differ substantially in their toxicity (Stanek et al. 2011, Kelly, Fussell 2012a). This has already resulted in current air pollution regulations which require monitoring of a number of air pollutants: fine PM fraction (PM_{2.5}), metals (lead, arsenic, cadmium, nickel), and B[a]P for which limit or target values for ambient concentrations have been set (Table 1, Table 2). There are currently no limit or target values for mercury, EC and OC.

The main current directives concerning air pollution are:

- Directive 2008/50/EC on ambient air quality for Europe, which sets limit values for ambient air concentrations of SO₂, NO₂, PM₁₀ and PM_{2.5}, lead (Pb), benzene (C₆H₆), carbon monoxide (CO), and Ozone (EUD (European Union Directive) 2008) (Table 1); The directive requires also monitoring of EC and OC.
- Directive 2004/107/EC which sets target values for the carcinogenic substances relating to arsenic, cadmium, nickel and benzo(a)pyrene in ambient air and defines requirements for mercury monitoring (Table 2.). (EUD (European Union Directive) 2005)

Table 1. The Air Quality Directive's limit values for air pollutants

Pollutant	Concentration	Averaging period	Permitted exceedences each year
Fine particles (PM _{2.5})	25 µg/m ³	1 year	n/a
Sulphur dioxide (SO ₂)	350 µg/m ³	1 hour	24
	125 µg/m ³	24 hours	3
Nitrogen dioxide (NO ₂)	200 µg/m ³	1 hour	18
	40 µg/m ³	1 year	n/a
PM ₁₀	50 µg/m ³	24 hours	35
	40 µg/m ³	1 year	n/a
Lead (Pb)	0.5 µg/m ³	1 year	n/a
Carbon monoxide (CO)	10 mg/m ³	Maximum daily 8 hour mean	n/a
Benzene	5 µg/m ³	1 year	n/a
Ozone	120 µg/m ³	Maximum daily 8 hour mean	25 days averaged over 3 years

Table 2. The Air Quality Directive's target values for air pollutants

Pollutant	Concentration	Averaging period	Permitted exceedences each year
Cadmium (Cd)	5 ng/m ³	1 year	n/a
Nickel (Ni)	20 ng/m ³	1 year	n/a
Polycyclic Aromatic Hydrocarbons	1 ng/m ³ (expressed as concentration of B[a]P)	1 year	n/a

1.2 Current air quality monitoring network in Europe and supersites

According to the directives, the current European air-monitoring network of air pollution consists of an extended number of monitoring sites where PM_{2.5} and NO₂ are monitored. In the European Union in 2014 there were: 2795 PM₁₀, 3077 NO₂ and 2128 O₃ monitoring sites with a data capture of at least 75 % per calendar year (EU-28 air pollution fact sheet 2014). There are four types of monitoring stations specified: traffic, urban, regional and other (with other sources of air pollution e.g. industry). B[a]P and metals concentrations are monitored at a more limited number of sites.

Within the European Union most air pollutants are analysed according to common standard methods. For instance, PM₁₀ and PM_{2.5} mass is measured according to EN 12341:2014 (CEN 2014b) standard; benzene according to EN 14662:2005 (CEN 2005a); EN 14211:2012 standard describes NO₂ analytical method (CEN 2012a); CO is determined according to EN 14626:2012 norm (CEN 2012b); EN 15549:2008 norm describes B[a]P measurement method (CEN 2008) and EN 14902:2005 metals determination (CEN 2005b).

In total there are 348 monitoring stations where B[a]P concentration is measured with 95 traffic, 183 urban, 44 regional and 26 other sites. In 2012, between 650 and 700 stations reported measurement data for each toxic metal (As, Cd, Pb and Ni).

In The Netherlands NO₂ is monitored at 76 and PM₁₀ at 74 sites. B[a]P and metals concentrations are monitored at 7 and 6 sites, respectively (AirBase - The European air quality database, Netherlands air pollution country fact sheet – 2014). In addition to the regular network for air pollution monitoring, there are also networks of monitoring sites providing extended knowledge on air quality in Europe. European Supersites for Atmospheric Aerosol Research (EUSAAR), Aerosols, Clouds, and Trace gases Research Infra Structure Network (ACTRIS) or The European Monitoring and Evaluation Programme (EMEP) are examples of such networks.

The EUSAAR/ACTRIS network

The EUSAAR network and since 2011 together with ACTRIS network coordinate 20 high-quality European ground-based stations (supersites) (Figure 1). The network's primary goal is to integrate the measurement of atmospheric aerosol properties and to ensure harmonization, validation, and data collection of long-term measurements of particle optical, physical and chemical properties, as these properties constitute the critical parameters for quantifying key processes and the impact of aerosols on climate and air quality. The monitoring network covers a variety of representative environments from clean maritime to polluted continental,

including several stations in extreme environments (e.g., arctic, high altitude) (Philippin et al. 2009).

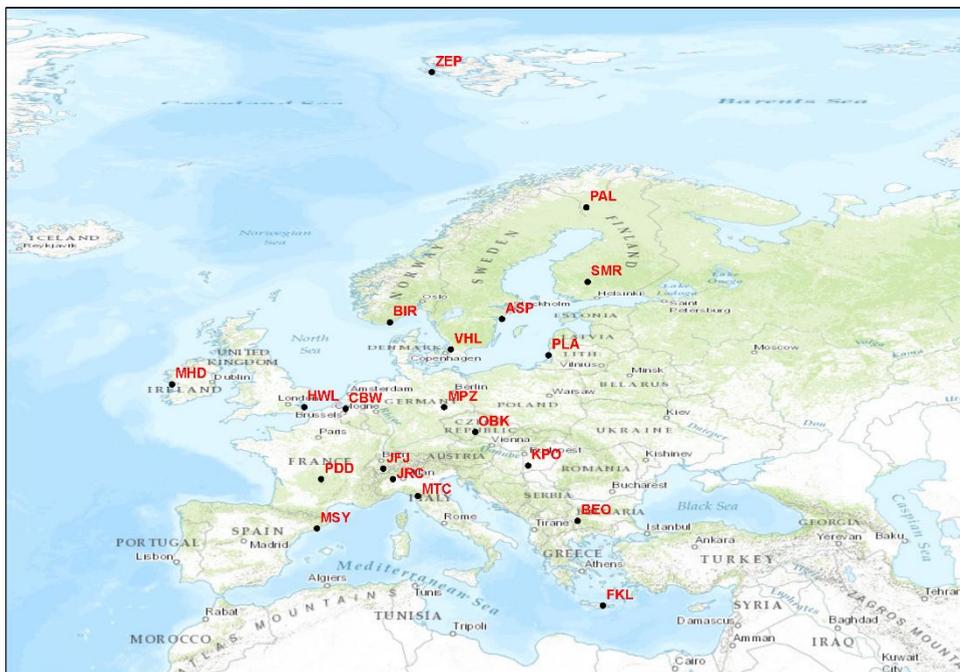


Figure 1. European EUSAAR/ACTRIS supersites (www.eusaar.net)

ASP	Aspvreten, Sweden	MEL	Melpitz, Germany
BEO	BEO Moussala, Bulgaria	MTC	Monte Cimone, Italy
BIR	Birkenes, Norway	MSY	Montseny, Spain
CBW	Cabauw, Netherlands	OBK	Kosetice, Czech Republic
FKL	Finokalia, Greece	PAL	Pallas, Finland
HWL	Harwell, United Kingdom	PDD	Puy de Dôme, France
JFJ	Jungfrauoch, Switzerland	PLA	Preila, Lithuania
JRC	JRC-Ispra, Italy	SMR	Hyytiälä, Finland
KPO	K-Pusztá, Hungary	VHL	Vavíhill, Sweden
MHD	Mace Head, Ireland	ZEP	Zeppelin, Spitsbergen, Norway

In the Netherlands the supersite is located in the small village Cabauw. The Cabauw Experimental Site for Atmospheric Research (CESAR) is situated in an agricultural area in the western part of The Netherlands, at a distance of 44 km from the North Sea and about 6 km from the nearest highway. The Cabauw station is located between the following cities: Utrecht NE, 20 km), Rotterdam (WSW, 30 km), The Hague (W 40 km) and Amsterdam (N, 40 km). Hence a variety of air masses can be encountered from clean maritime to continental polluted air. The Cabauw observatory is owned and supervised by the Royal Netherlands Meteorological Institute (KNMI). In Cabauw the following regulated pollutants are continuously monitored: CO, NO, NO₂, O₃, PM₁₀, PM_{2.5}, and SO₂. At the Cabauw site, a 213 m high mast is used for meteorological research to establish relations

between the state of the atmospheric boundary layer, land surface conditions and the general weather situation for all seasons. Further, Cabauw contributes to extensive atmospheric research, including land-atmosphere and cloud, aerosol and radiation interactions. On the site are also well-kept observation fields for micrometeorological observations, including soil heat flux, soil temperatures and various radiation measurements. Remote sensing observations are mostly performed at the Remote Sensing Site located 300 m SSE of the main tower. A scanning X-band radar operated by Delft University of Delft is located on top of the tower. Particle size distributions are measured with an Aerosol Particle Sizer and a Scanning Mobility Particle Sizer. Details on ongoing measurements can be found on: www.cesar-observatory.nl.

The EMEP programme

Initially, The European Monitoring and Evaluation Programme (EMEP) focused on assessing the transboundary transport of pollutants to assess acidification and eutrophication (sulphur dioxide (SO₂), nitrogen oxides (NO_x) and ammonia (NH₃) (Tørseth, Aas, 2012). Most of SO₂ and NO_x is emitted to the atmosphere by the combustion of fossil fuel in electricity generating power stations, industrial plants, residential heating, commercial and service sectors. Road transport, shipping and aircraft are significant sources of NO_x emissions as well. NH₃ emissions are related to agricultural activities such as storage of manure, soil fertilizing and animal husbandry. Later, the scope of the programme was widened to address the formation of ground level ozone and, more recently to persistent organic pollutants (POPs), heavy metals and particulate matter.

The EMEP monitoring sites are located such that significant local influences (local emission sources, local sinks, topographic features, etc.) are minimized. The basic idea is that the data should be representative for a larger region. The monitoring methods used in EMEP are chosen based on a compromise between several criteria: a sufficient precision is needed at low concentration levels, and the method should be robust and simple to apply in the field. If adequate international standards are available from Comité Européen de Normalisation (CEN) or World Meteorological Organization (WMO), EMEP applies those methods. There are some exceptions, for example if CEN standards are applicable for higher concentrations of pollutants (e.g. in urban areas), the methods may be inadequate at EMEP sites having low concentrations. Where reference methods are not available, EMEP has developed its own methodologies. In addition to applied reference methods and standard operation procedures, EMEP conducts laboratory and field intercomparison of most components defined by the monitoring programme (Tørseth et al. 2012). Presently, more than 300 monitoring stations in 42 countries participate in the EMEP network.

The EMEP programme relies on three main elements: (1) collection of emission data, (2) measurements of air and precipitation quality and (3) modelling of atmospheric transport and deposition of air pollution. Through the combination of these three elements, EMEP fulfils its required assessment programme and regularly reports on emissions, concentrations and deposition of air pollutants, the quantity and significance of transboundary fluxes and related exceedances of critical loads and threshold levels. The combination of these components provides also a good basis for the evaluation and qualification of the EMEP estimates. The EMEP programme is carried out in collaboration with a broad network of scientists and national experts that contribute to the systematic collection, analysis and reporting of emission data, measurement data and integrated assessment results. Both, EMEP and EUSAAR networks consist of regional background or even remote sites and therefore have limited use for human exposure assessment.

1.3 Should European air quality monitoring network be expanded?

Based on the available knowledge of individual air pollutants and adverse health effects caused by those pollutants I will discuss the merits of expanding the air pollution monitoring with additional PM components. Extended air quality monitoring should broaden our knowledge of spatial contrasts and may impact on specific sources of air pollution and their control by regulation of specific sources (e.g. wood smoke).

1.3.1 Health effects of PM composition

Human exposure to air pollution causes adverse health effects (Brunekreef, Holgate 2002, Pope, Dockery 2006). The most common indicator of air quality is the concentration of particulate matter with diameters smaller than 10 or 2.5 μm (PM₁₀, PM_{2.5}, respectively). However, PM is a chemically complex mixture and it has been suggested that observed adverse health effects may depend on PM chemical composition (Stanek et al. 2011, Kelly, Fussell 2012b). Epidemiological studies have started to assess elemental composition of particles, but few studies have assessed the relationship between organic components and adverse health effects. Epidemiological studies have applied two approaches to gain insight in health effects of different PM components. In the first approach, measurements of individual components (elements, organic components) are used directly as an exposure variable in an epidemiological analysis. This approach is applied in studies of short term as well as long term effects of various PM components. Exposure for short-term studies is typically characterized by measurements at central sites. The second approach is to apply source apportionment methods using the chemical composition of particles. In this approach the health effects of

particles apportioned to the identified sources (such as traffic, wood smoke, soil, secondary sulfate, oil combustion) are studied.

There are numerous publications on toxicological effects of PM components obtained in *in vitro* or *in vivo* experiments. There is some information on effects of short-term exposure to PM components, exploiting networks with PM composition measurements such as the US Improve network (Vedal et al. 2013). However, due to limited data on the spatial distribution of population exposure to organic components or to particles from sources other than traffic (e.g. woodsmoke), there is limited knowledge on long-term effects of those components (Kelly, Fussell 2012a).

Recently, several papers were published which reviewed the current knowledge on adverse health effects of PM composition or pollution from specific sources (Naeher et al. 2007, Kim et al. 2013, WHO 2013).

OC

There is an increasing number of studies on the associations of organic carbon with health. Organic carbon has been included in epidemiological studies less often than black carbon. In most published studies, short-term effects of exposure to organic carbon were investigated. Organic carbon was associated with short-term cardiovascular effects (Delfino et al. 2010c, Kim et al. 2012, Zanobetti et al. 2009), cardiovascular mortality (Mar et al. 2000, Ostro et al. 2007), respiratory health effects (Kim et al. 2008), or with changes in the levels of inflammatory markers (Hildebrandt et al. 2009). Within a Dutch project RAPTES, OC, together with nitrate and sulfate, was found to be associated with markers of systemic inflammation in a semi-experimental study (Strak et al. 2013).

A very limited number of studies have investigated associations between long-term exposure to organic carbon and adverse health effects. The California Teachers Study (CTS), a prospective cohort study, investigated association between PM_{2.5} constituents and total and cardiopulmonary mortality (Ostro et al. 2011). For organic carbon, associations were observed for both ischaemic heart disease and pulmonary mortality, whereas elemental carbon was only associated with ischaemic heart disease mortality (Ostro et al. 2011). Moreover, a forward-selection regression analysis indicated that long-term exposures to OC and SO₄, in particular, had stronger associations with all four outcomes than did the other constituents or PM_{2.5} mass.

In a recent American epidemiologic study, cohort data from two studies — the Multi-Ethnic Study of Atherosclerosis (MESA) and the Women's Health Initiative–Observational Study (WHI-OS) — were used to investigate subclinical markers of atherosclerosis and clinical cardiovascular events in relation to PM_{2.5} mass and a number of PM_{2.5} components including OC. In the MESA cohort data, OC together with PM_{2.5} and sulfur were strongest associated with increased carotid intima-media thickness (CIMT). Similarly, in the WHI-OS cohort data, evidence for

associations with incidence of cardiovascular mortality and cardiovascular events was found to be good for OC and sulfur, respectively, and for PM_{2.5} (Vedal et al. 2013).

Due to a lack of data, epidemiological studies have not been able to separate primary and secondary organic particles (WHO 2013). A number of studies have reported that while total organic carbon was not associated with the outcomes, associations have been observed for primary organic carbon (and not secondary organic carbon compounds) (Delfino et al. 2009, Delfino et al. 2010b, Delfino et al. 2010a). In one study, primary organic carbon was associated with markers for systemic inflammation, whereas secondary organic carbon was associated with a marker for pulmonary inflammation (Delfino et al. 2010c).

While evaluating results of studies on adverse health effects of organic carbon it should be remembered that organic carbon is a very complex mixture of primary and secondary organic aerosols that may contain specific components with various health outcomes, such as PAH. As a result the health impact of organic carbon characterized by OC mass may vary from site to site and time to time.

Another challenge in assessment of adverse health effect of exposure to organic carbon in epidemiological studies is the separation of the effects of combustion-derived organic carbon from those of black carbon and/or elemental carbon because of a high correlation due to the common source: combustion processes (WHO 2013).

PAH

PAH's carcinogenic and toxicological properties have been extensively investigated and reviewed in the last decades (Nielsen et al. 1996, Kim et al. 2013, Luch 2005). Their mode of action is genotoxic. They also induce aberrant gene expression and cell signaling and epigenetic effects that may contribute to their carcinogenic and other toxicological properties. Benzo(a)pyrene has been classified as a human carcinogen (class 1) by the International Agency for Research on Cancer (IARC, 2015 <http://monographs.iarc.fr/ENG/Classification/>). Various other PAHs have been classified as a possible human carcinogen (class 2B, such as chrysene and naphthalene).

PAH have been associated with various short term adverse health effects (Kim et al. 2013). Exposure to PAH was linked with elevated risk of short-term respiratory health problems such as asthma or respiratory allergic disease (Delfino 2002, Diaz-Sanchez et al. 1994). Traffic emission sources of organic chemicals represented by PAH were found to be associated with increased systemic inflammation (Delfino et al. 2010b). Another study found an association between PM, particle-bound organic compounds (including PAH) and cardiovascular symptoms (e.g. heart problems, shortness of breath) in survivors of myocardial infarctions (Kraus et al. 2011).

A substantial number of occupational epidemiological studies presented evidence of adverse health effects related to long-term exposure to PAH (Kim et al. 2013). Elevated risk of mortality, lung, bladder, gastrointestinal cancers, ischemic heart disease has been associated with employment in jobs that entail exposure to polycyclic aromatic hydrocarbons (PAH) such as aluminum smelting, chimney sweeping, waste incineration, motor vehicle operators, bakers, and tar distillation (Burstyn et al. 2005, Kim et al. 2013).

Some studies have examined the adverse effects of PAH exposure on children's cognitive and brain development (Jedrychowski et al. 2003, Peterson et al. 2015a, Choi et al. 2012). Perera et al. found an association of levels of PAH-DNA adducts in cord blood with higher symptom scores of anxiety and depression measured at 4.8 years (Perera et al. 2011). In the same cohort, prenatal exposure to benzo[a]pyrene measured from maternal personal air quality monitoring (at a median level of 2.27 ng/m³), and also cord blood adduct levels, were associated with these effects, as well as attention problems at age 6–7 years (Perera et al. 2012). Similar findings were reported from a study of children in Poland (Edwards et al. 2010), where high PAH exposure in utero also restricted fetal growth (Choi et al. 2012). Another, recent American study found a positive relation between exposure to PAH air pollutants to slower processing speed, attention-deficit/hyperactivity disorder symptoms, and externalizing problems in urban youth by disrupting the development of left hemisphere white matter (Peterson et al. 2015b). In addition the authors suggest that postnatal PAH exposure contributes to additional disturbances in the development of white matter in dorsal prefrontal regions.

Several other studies reported evidence of elevated risk of respiratory adverse health effects in children related to prenatal exposure to PAH (Salvi 2007). A Polish study that investigated the association between exposure to ambient PAH during pregnancy and the prevalence of respiratory symptoms during the first year of life, reported a 4.8-fold increased risk of cough, 3.8-fold increased risk of wheeze without cold and an 82% increased risk of runny or stuffed nose with increased maternal exposure to PAH, suggesting that prenatal exposure to air pollutants has a significant impact on respiratory health in newborns (Jedrychowski et al. 2005). Similar observations were reported by Miller et al. in a New York study (Miller et al. 2004). The authors additionally indicated a higher prevalence of reported asthma in children by the age of 2 years, when mothers were exposed to high levels of PAH during pregnancy. These results suggest that early exposure to airborne PAH could lead to increased respiratory symptoms and to the development of asthma by the age of 12–24 months. A recent Polish study has investigated the long term effects of prenatal and postnatal airborne PAH exposures on ventilatory lung function of non-asthmatic preadolescent children in a prospective birth cohort study in Krakow, with the conclusion that transplacental exposure to PAH compromises

the normal developmental process of respiratory airways and that this effect is compounded by postnatal PAH exposure (Jedrychowski et al. 2015).

Within the recent WHO project: “Review of evidence on health aspects of air pollution – REVIHAAP”, studies on PAH exposure and their health effects were reviewed. The authors based their assessment on recent studies on health effects of PAH exposure. Despite of new links between PAH exposure and cardiovascular end-points, they cannot be convincingly separated from the effects of particle mass and therefore cannot impact on the target values presently used ($1\text{ng}/\text{m}^3$ for B[a]P). Further, the authors discussed the use of B[a]P as a single, carcinogen indicator representing the carcinogenic potential of PAH mixture. There is an agreement that the monitoring of single PAH (B[a]P) may lead to underestimation of the carcinogenic potential of airborne PAH mixtures. Recent analyses showed relatively constant ratio between B[a]P and dibenzo[a,l]pyrene (one of the most potently carcinogenic PAH). Moreover, dibenzo[a,l]pyrene has not been tested for carcinogenicity by inhalation. Those arguments led to agreement of not changing current PAH monitoring requirements (WHO 2013).

Woodsmoke

A systematic review of the health effects of particles from biomass combustion concluded that there was no reason to consider PM from biomass combustion less harmful than particles from other urban sources, but that there were fewer studies investigating the adverse health effects of biomass combustion (Naeher et al. 2007).

A number of published 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.

Exposure to woodsmoke is associated with acute and short term effect on human health. Barregard et al found an inflammatory response and signs of increased oxidative stress in the respiratory tract, especially in the lower airways caused by woodsmoke at levels that can be found in smoky indoor environments (Barregard et al. 2008).

A few studies based on source apportionment provided comparison between short-term health effects of particles from biomass combustion and particles from traffic. In a study conducted in Copenhagen (Andersen et al. 2007), particles from biomass combustion were positively correlated with cardiovascular and respiratory hospital admissions, whereas particles from traffic were not. In Atlanta, Georgia (Sarnat et al. 2008), woodsmoke was associated with cardiovascular emergency department visits as strongly as was traffic, but neither of the sources was associated with respiratory health. In Phoenix, Arizona (Mar et al. 2006), wood combustion was associated with cardiovascular mortality, with effect estimates slightly lower than those for traffic particles. Finally, in Spokane, Washington

(Schreuder et al. 2006), associations with cardiovascular mortality were of similar strength for biomass combustion and traffic.

Long-term exposure to biomass PM from indoor use has been associated in low-income countries, for example, with lower respiratory infections (including pneumonia) in children, chronic obstructive pulmonary disease in women, and lung cancer (WHO 2013).

There are very few studies on the health effects of longer-term exposure to outdoor woodsmoke. In British Columbia, Canada, exposure to woodsmoke was associated with an increased risk of infant bronchiolitis, but not with the development of childhood asthma (Clark et al. 2010, Karr et al. 2009). In California, PM_{2.5} from biomass combustion was associated with preterm birth, but not with low birth weight (Wu et al. 2011, Wilhelm et al. 2012).

Woodsmoke in the Netherlands is associated with significant annoyance due to the smell and associated fear of health effects in communities. The growing evidence of adverse health effects caused by woodsmoke results in growing social pressure on policymakers to regulate, limit or even prohibit the use of biomass fuel in household stoves and fireplaces used for cooking, recreation or domestic heating (Butter, Keij 2006).

Overall, there is strong evidence for health effects related to PAH and woodsmoke. The evidence base for the generic marker OC is weaker, but growing. The growing evidence of adverse, health effects of exposure to PM components, is a valid argument for an extension of air quality monitoring. More extensive monitoring increases the feasibility of epidemiological studies evaluating new pollutants.

1.3.2 Spatial and temporal variation of PM organic pollutants

Knowledge on spatial and temporal variation of concentrations is needed to design a network, to decide on the number of sites needed in a network (more than one per city?), distribution over site types and seasons (in case of non-automatic monitors).

OC

In our study, OC concentrations across Europe exhibited similar patterns to those of NO_x, PM and PM absorbance that were reported before (Eeftens et al. 2012b, Cyrus et al. 2012) (Chapter 2). Although the trend of OC concentrations across Europe was similar to the trend of traffic related markers, the OC contrast within most of study areas differed substantially from other pollutants (Chapter 2). It is well documented that OC can originate from multiple sources (Saarikoski et al. 2008). The higher OC concentrations in southern European study areas may have been caused by higher secondary organic aerosol (SOA) formation due to more intensive oxidation of gas-phase compounds that occurs at higher temperatures (Sillanpää et al. 2005) and was not necessarily due to heavier traffic (which is the

reason of higher concentration of traffic related markers in this part of Europe). This is supported by inconsistent spatial correlation between OC and traffic related markers in the individual study areas, ranging from 0.21 to 0.83, without clear trend. There was also substantial variability found for OC/PM_{2.5} and OC/EC ratios for individual sites across Europe. OC/PM_{2.5} varied between 0.04 and 0.36, while OC/EC varied between 0.6 and 4.4.

We found that the largest variability in street to urban background (S/UB) ratios occurred with OC concentrations. In some countries there was almost no difference between S and UB location (Oslo, Copenhagen, The Netherlands) while in other countries the difference was larger and more significant (London/Oxford, Catalonia) (Chapter 2). Even larger variation across Europe was found in the regional to urban background (RB/UB) ratios. In several areas RB was higher than UB (London/Oxford, Munich/Augsburg, Catalonia) and in other areas much lower (Athens, Oslo). This may be caused by presence of a specific OC source in the neighbourhood of the sampling site such as combustion of biomass, which may be more common in rural areas.

The seasonal differences in most pollutant concentrations have been presented in previous studies (Gehrig, Buchmann 2003, Menichini et al. 2007). The reasons for higher concentrations of air pollutants in winter include higher pollutant emissions (due to heating) and poorer dispersion because of less vertical mixing during winter. Viana et al. has reported seasonal differences of OC and EC in Barcelona. In comparison with that study we found in Catalonia a slightly higher cold/warm ratio for OC - 2.22 in comparison to 1.76 (Viana et al. 2007). The EC cold/warm ratio was a bit lower in our study than was reported by Viana et al. (1.43 and 1.65, respectively).

PAH

In our study PAH exhibited a different trend in concentrations across Europe than the traffic markers, PM_{2.5} or OC, with similar concentrations in southern and northern European study areas.

The PAH S/UB ratio was overall smaller than for EC, probably as a result of the larger contribution of other combustion sources than those of traffic (wood burning, industrial) to PAH concentrations relative to EC. Differences in dispersion are unlikely between PAH and EC, as both pollutants are primarily in sub-micrometer particles. The variation of PAH S/UB ratios across Europe may reflect the variation of the motorised traffic contribution relative to other PAH sources across countries. In general in southern Europe, the S/UB was higher consistent with traffic being a relatively more important source of PAH in southern Europe. A formal source apportionment, however, was not conducted.

It was previously reported that particle-bound PAH show larger seasonal differences than gas phase PAH (Schauer, Niessner & Poschl 2003, Prevedouros,

Jones & Sweetman 2004, Prevedouros et al. 2004). Heavier PAH are mostly emitted during heating processes, lighter PAH are associated more with traffic emissions. In agreement with those results in our study seasonal differences were found for all pollutants. Particle-bound PAH showed the large seasonal differences, adding to the evidence that non-traffic combustion sources contribute significantly to PAH concentrations (Prevedouros et al. 2004). Prevedouros et al. (2004) compared seasonality of PAH in a number of locations (UK, Sweden, Finland, Arctic Canada) between 1991 and 2000. In agreement with our results (chapter 2), the highest cold to warm ratios of individual PAH were found in Scandinavian countries (above 30). Prevedouros et al. (2004) found an average B[a]P cold/warm ratio in London of 5.1 while in our study in London/Oxford this ratio was 18.16 (chapter 2).

Levoglucon

The large variability in average levoglucon concentrations in our study (Chapter 4) is consistent with the previously reported substantial differences in levoglucon for different sites across Europe (Caseiro, Oliveira 2012, Reche et al. 2012, Pio et al. 2008). The comparison is limited as studies differ widely in terms of season of measurement. Most studies are completed in winter, in one particular winter month or during forest burning periods. The substantial 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 monitoring location. In our study (Chapter 4), the range to mean ratio of levoglucon annual average concentration within four study areas varied from 132% to 560%, illustrating large within area variability. As for traffic-related air pollution, intra-urban exposure estimates are needed.

Higher levoglucon 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 levoglucon in winter include higher pollutant emissions (domestic wood burning heating systems) and poorer dispersion because of less vertical mixing during winter. As the cold/warm season ratios for levoglucon are substantially higher (median = 6.3 – Chapter 4) than observed for traffic-related pollutants (EC median ratio 1.27 – Chapter 2) for which source strength does not show much seasonal variation, increased source strength appears to contribute most to the levoglucon increases in the cold season.

OP

In our study, OP DTT levels were highest in southern study areas (Chapter 5), but the differences between the three southern and the three northern study areas were smaller (south/north ratio = 1.5) than we found for traffic-related pollutants

including NO₂, and EC (south/north ratio – 2.2) and for PM_{2.5} mass (south/north ratio – 2.1) ,(Eeftens et al. 2012b, Cyrus et al. 2012, Jedynska et al. 2014b).

The smaller contrast across Europe (attributed partly to differences in traffic emissions) is consistent with the small difference between street and urban background locations found in this study (median S/UB=1.10). Several studies have recently shown that the DTT oxidative potential assay exhibits rather modest contrasts between different sites within a study area (Yang et al. 2015, Janssen et al. 2014, Hu et al. 2008). OP DTT street/urban ratios that were recently reported: 1.2 (Janssen et al. 2014, Yang et al. 2015), 1.3 (Hu et al. 2008) or 1.1 in our study (Chapter 5) are comparable or even lower than the ratios for PM_{2.5} (1.2) (Eeftens et al. 2012b). This suggests that measurement of OP DTT will not be very useful for studies evaluating health effects related to proximity to major roads.

In our study, in most study areas we found higher OP DTT levels during cold period than those found in the warmer period of a year(Chapter 5). The median cold/warm ratio was 1.51. A similar cold/warm ratio, 1.59, has also been previously reported by Saffari et al. in an American study (Saffari et al. 2014). Another American study presented smaller differences in DTT levels between seasons in several locations (winter/summer ratio = 1.2) (Vedal et al. 2013). In our study we used similar extraction method and we used also quartz filters for the sampling which makes comparison of the results easier. The OP DTT cold to warm ratio of 1.51 was lower than the ratio found for levoglucosan (6.3), a marker of wood combustion, with known high seasonality and ΣPAH (4.5), which are also influenced by more intensive domestic heating during winter (Jedynska et al. 2014b). The OP DTT cold to warm ratio was similar as the ratio for OC, which has various primary and secondary sources (1.9), and EC, used as traffic marker (1.3). For air pollutants with traffic as a dominant source, emissions do not differ much between winter and summer and the higher concentration ratios are largely due to poorer dispersion conditions. Our cold/warm increases suggest that emission of components to which the DTT assay responds were fairly constant across seasons as well.

1.3.3 Specificity of individual air pollution markers (OC, OP, PAH, levoglucosan) and their correlation with PM mass and elements

In terms of choosing additional air pollutants for routine air quality monitoring we need to consider the specificity of the individual PM markers. Markers may be a specific component (levoglucosan, benzo[A] pyrene) or represent a group of components (OC) or even a (biologically relevant) generic property of PM (OP). We can identify pollutants with multiple sources (e.g. PAH, OC, OP) and markers representing specific sources (e.g. levoglucosan) which might be useful to assess the population exposure to emissions from individual, specific sources (e.g. specific industrial sources, biomass combustion).

PM components considered for inclusion to routine air quality network should preferably not be highly spatially correlated with pollutants already included in the routine network. A high spatial correlation between considered new pollutants and already measured pollutants limits separation of long term health effects of these new pollutants from those already included in a number of epidemiological studies (PM mass, PM₁₀, NO₂) within a single study area. However, a high correlation with already measured / regulated pollutants does not necessarily imply that a new pollutant may not be relevant to include in air quality assessment. If the ratio between its concentration and concentrations of already monitored pollutants differs between different study areas and the new pollutant is the true causal agent, one should expect the estimated health effect of the new pollutant to be more consistent between different study areas than the standard pollutant. Evaluation of epidemiological studies in multiple study areas is needed to investigate this issue.

PAH are affected by a broad range of processes of incomplete combustion of organic substances. PAH's sources include: domestic, transportation, industrial, agricultural and natural processes. (Maliszewska-Kordybach 1999, Ravindra, Sokhi & Van Grieken 2008).

OC is a mixture of many groups of compounds originating from primary sources and secondary formation processes. Major anthropogenic emission sources are biomass and fossil fuel combustion. Anthropogenic biomass combustion includes both the agricultural combustion such as burning of biomass for land clearing and the combustion for heat production, e.g. in domestic boilers, wood stoves and fireplaces. A large fraction of organic aerosol is formed in the atmosphere from low-volatility compounds produced by the oxidation of gas-phase anthropogenic and biogenic precursors e.g. volatile organic compounds – VOC. There is relatively little information available on the contribution of secondary OC to total OC mass in Europe, but some studies showed that the secondary organic aerosol (SOA) might contribute up to 80% of OC mass, especially in summer (Saarikoski et al. 2008, Castro et al. 1999). The complexity of OC origin means that routine monitoring of OC will not give us information of specific air pollution sources but will serve as a generic indicator of a possibly significant class of PM components.

Levoglucosan is a well-accepted tracer for wood burning in ambient air (Simoneit 1999). 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).

Oxidative potential (OP) is an unspecific metric of air pollution and is dependent on PM components origins and on the OP determination method. There are a few assays e.g. ESR or antioxidant depletion assay (AA) which are sensitive to the transition metals Fe, Cu (Yang et al. 2014). Other OP assays include DTT or CRAT

that are both sensitive to a broad range of PM constituents (organic pollutants and metals), and consequently makes the resulting OP measurements unspecific markers for air pollution (Yang et al. 2014, Zomer et al. 2011).

Correlation between PAH, OC, levoglucosan, OP and other air pollutants

Most studies reported temporal correlation between pollutants. Temporal correlations between pollutants are often high and are driven by meteorological conditions which are mostly contributing to highest concentrations in winter for most pollutants. Within the ESCAPE project we had an unique chance to determine spatial correlations between our organic pollutants and pollutants that are commonly measured in standard ambient air quality monitoring. We further evaluated correlations with eight key elements in ten study areas across Europe.

As described in Chapter 2 the spatial correlation between **OC, B[a]P** and PM mass and NO₂ is only moderate and varies substantially across Europe. This means that OC and B[a]P represent other sources and add extra characterization of air pollution exposure, that is not represented by pollutants that are already monitored. To our knowledge there are no studies reporting large-scale spatial correlation between PAH, OC and other pollutants. In our study we found large variation in spatial correlations between PAH, OC and other components, suggesting various sources of PAH and OC at individual sites (traffic, wood combustion). Correlations between PAH, OC and pollutants often used as traffic markers (EC, PM_{2.5}abs, NO₂) varied significantly across Europe. Correlation between OC and NO_x varied between 0.21 and 0.83. The range of PAH and NO_x correlation was even larger (from 0.03 to 0.77). Analyses of correlation between PAH and other pollutants confirmed the influence of different sources on PAH concentrations. That conclusion was based on the clear trend of PAH correlations with levoglucosan (specific wood smoke marker) and hopanes/steranes (traffic marker) in the different study areas. In Oslo, The Netherlands and Munich/Augsburg PAH correlated with levoglucosan significantly. The correlation with levoglucosan was higher than the correlation with hopanes/steranes. In Catalonia PAH correlated highly with hopanes/steranes while it did not correlate with levoglucosan.

There were only low to moderate correlations between organic pollutants and the 8 key elements in PM_{2.5} and PM₁₀ evaluated in ESCAPE (Table 3, 4). We calculated the correlation with elements, as elemental composition is easier and cheaper to measure than specific organic components. PAH were moderately correlated with Cu, Fe and Zn, probably reflecting the common traffic source (Table 3, Table 4). Correlations were higher with PM₁₀ than PM_{2.5} elemental concentrations, consistent with Cu, Fe and Zn deriving from non-tailpipe (coarse particle) emissions. Chrysene had the highest correlation with Cu and Fe. OC

correlations with Cu, Fe, Zn were between 0.4 and 0.5, lower than for PAH, likely related to the larger secondary particle fraction of OC compared to PAH. The substantial fraction of OC from secondary origin also explains moderate correlation between OC and PAH and levoglucosan. PAH and levoglucosan are primarily primary pollutants.

Based on the observed correlations between PAH, OC and levoglucosan and other pollutants we can conclude that there is no other PM component with the same spatial variability and it is not possible to use other markers to capture PAH, OC and levoglucosan spatial contrasts.

Table 3. Median, minimum and maximum Spearman correlation between organic and elemental pollutants in PM_{2.5} per study area

	PM _{2.5} Cu	PM _{2.5} Fe	PM _{2.5} K	PM _{2.5} Ni	PM _{2.5} S	PM _{2.5} Si	PM _{2.5} V	PM _{2.5} Zn
B[a]P	0.50 -0.04 – 0.73	0.46 0.08 – 0.73	0.40 -0.16 – 0.65	0.13 -0.45 – 0.79	0.16 -0.42 – 0.47	0.37 0.04 – 0.65	0.18 -0.28 – 0.71	0.32 -0.04 – 0.88
Chrysene	0.64 -0.02 – 0.75	0.65 0.09 – 0.72	0.35 -0.13 – 0.63	0.21 -0.33 – 0.75	0.21 -0.40 – 0.43	0.42 0.07 – 0.61	0.21 -0.13 – 0.68	0.34 0.16 – 0.86
ΣPAH	0.55 -0.03 – 0.69	0.49 0.09 – 0.68	0.40 -0.09 – 0.65	0.15 -0.41 – 0.81	0.19 -0.45 – 0.44	0.31 0.01 – 0.59	0.16 -0.22 – 0.74	0.33 0.06 – 0.86
EC	0.79 0.64 – 0.97	0.81 0.56 – 0.97	0.31 -0.17 – 0.60	0.28 -0.22 – 0.62	0.39 -0.07 – 0.57	0.54 0.24 – 0.82	0.30 -0.20 – 0.61	0.62 0.32 – 0.91
OC	0.42 0.10 – 0.66	0.43 0.16 – 0.60	0.30 0.07 – 0.63	0.15 -0.35 – 0.55	0.33 -0.18 – 0.76	0.26 0.10 – 0.58	0.10 -0.48 – 0.46	0.28 0.06 – 0.65
Levoglucosan*	-0.25 -0.43 – 0.47	-0.24 -0.40 – 0.51	0.32 -0.15 – 0.57	-0.41 -0.76 – 0.81	0.10 -0.48 – 0.18	-0.09 -0.29 – 0.24	-0.37 -0.62 – 0.73	0.08 -0.61 – 0.58
ΣHopanes/ Steranes*	0.46 0.31 – 0.75	0.48 0.29 – 0.76	0.32 -0.27 – 0.37	0.42 0.28 – 0.58	0.36 -0.10 – 0.51	0.27 -0.10 – 0.56	0.35 -0.25 – 0.42	0.35 0.32 – 0.47
OP DTT	0.12 -0.39 – 0.40	0.13 -0.37 – 0.35	0.09 -0.27 – 0.60	0.06 -0.29 – 0.49	0.02 -0.38 – 0.65	0.02 -0.36 – 0.42	0.26 -0.21 – 0.43	0.14 -0.28 – 0.51

* four study areas instead of ten

Table 4. Median, minimum and maximum Spearman correlation between organic and elemental pollutants in PM₁₀ per study area

	PM ₁₀ Cu	PM ₁₀ Fe	PM ₁₀ K	PM ₁₀ Ni	PM ₁₀ S	PM ₁₀ Si	PM ₁₀ V	PM ₁₀ Zn
B[a]P	0.57 0.04 – 0.82	0.53 0.01 – 0.77	0.46 -0.07 – 0.71	0.31 -0.09 – 0.75	0.26 -0.32 – 0.66	0.45 -0.10 – 0.71	0.28 -0.10 – 0.79	0.39 0.22 – 0.80
Chrysene	0.71 0.06 – 0.85	0.71 0.02 – 0.81	0.51 0.11 – 0.75	0.38 0.07 – 0.77	0.36 -0.29 – 0.64	0.50 -0.03 – 0.74	0.30 0.01 – 0.85	0.53 0.22 – 0.80
ΣPAH	0.58 -0.02 – 0.82	0.53 0.03 – 0.74	0.43 -0.06 – 0.78	0.33 -0.03 – 0.76	0.28 -0.33 – 0.67	0.39 -0.14 – 0.75	0.25 -0.06 – 0.80	0.40 0.21 – 0.77
EC	0.89 0.62 – 0.96	0.85 0.62 – 0.96	0.50 0.17 – 0.74	0.52 0.11 – 0.75	0.47 0.05 – 0.64	0.68 0.43 – 0.82	0.33 -0.02 – 0.86	0.74 0.60 – 0.90
OC	0.45 0.18 – 0.64	0.47 0.19 – 0.64	0.43 0.27 – 0.72	0.27 -0.18 – 0.60	0.27 -0.12 – 0.66	0.37 0.22 – 0.48	0.20 -0.28 – 0.52	0.42 0.24 – 0.69
Levoglucosan*	-0.29 -0.38 – 0.63	-0.22 -0.33 – 0.49	0.12 -0.29 – 0.54	-0.44 -0.54 – 0.73	-0.08 -0.34 – 0.54	-0.13 -0.33 – 0.40	-0.38 -0.49 – 0.67	0.01 -0.57 – 0.56
ΣHopanes Steranes*	0.52 0.34 – 0.73	0.53 0.21 – 0.73	0.31 0.12 – 0.49	0.34 0.27 – 0.77	0.31 0.10 – 0.71	0.33 0.15 – 0.45	0.31 -0.14 – 0.38	0.57 0.31 – 0.60
OP DTT	0.12 -0.50 – 0.30	0.14 -0.42 – 0.30	0.06 -0.28 – 0.53	0.15 -0.15 – 0.41	0.08 -0.38 – 0.46	0.01 -0.46 – 0.44	0.20 -0.31 – 0.49	0.12 -0.37 – 0.63

* four study areas instead of ten

Levoglucosan

To our knowledge there are no studies reporting spatial correlations between levoglucosan and other pollutants. In our study we investigated spatial correlation between levoglucosan and other pollutants within 4 European study areas (Oslo, The Netherlands, Munich and Catalonia). Levoglucosan correlated the highest with Σ PAH and B[a]P (0.51–0.89). Wood burning is known to be one of the PAH sources (Ravindra, Sokhi & Van Grieken 2008). The correlation with Σ PAH was highest in Oslo and lowest in Catalonia, probably relating to a combination of higher wood smoke emissions and lower traffic emissions in Oslo. This interpretation is consistent with the higher correlation between Σ PAH and traffic markers in Catalonia (Jedynska et al. 2015). The correlation between levoglucosan and PM_{2.5}, EC and OC was low to moderate. In the Flanders (northern Belgium) study, the patterns of average concentrations were also different for levoglucosan versus EC, OC and PM_{2.5} (Maenhaut et al. 2012).

The correlation between levoglucosan and potassium (K) in PM_{2.5}, which is used as a biomass combustion marker as well, was relatively low ($-0.15 < r < 0.57$, with median of 0.32). The correlation between levoglucosan and K in PM₁₀ was even lower (median $r=0.12$), probably reflecting the impact of soil derived K. The low spatial correlation may be due to more sources than wood burning contributing to potassium levels (Pio et al. 2008, Puxbaum et al. 2007, Caseiro et al. 2009). Other sources of potassium include soil, seaspray, meat cooking and waste incinerators (Giannoni et al. 2012). Furthermore, we measured total potassium 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 potassium as reflecting wood burning emissions.

OP

A limited number of studies reported spatial correlation between OP and other pollutants. Previous studies mostly reported temporal correlation between OP and other components. Several studies presented high temporal correlation between DTT and PM_{2.5} (Janssen et al. 2014, Yang et al. 2014). The DTT assay is known to be sensitive to organic compounds (mainly quinones) (Cho et al. 2005) but also an interaction between DTT and the water soluble metals was found (Ntziachristos et al. 2007).

Two published studies have reported spatial correlation between OP DTT and other air pollutants (Yang et al. 2015, Saffari et al. 2014). Saffari et al assessed spatial correlation for different seasons between OP DTT of quasi-ultrafine particles (PM_{0.25}) at ten locations across the Los Angeles Basin, and found across seasons the highest correlations between DTT activity and carbonaceous PM (Pearson's $R > 0.70$ for OC, both soluble and insoluble). Correlations between OP DTT and PM

composition varied depending on the season, with the highest correlations occurring during winter (Saffari et al. 2014).

Yang et al. (Yang et al. 2015) reported spatial correlation between OP DTT and traffic markers (PM absorbance, NO_x), PM mass and PM elemental composition for 40 sites in The Netherlands. The authors found moderate correlations between OP DTT and PM_{2.5} ($r = 0.56$). OP DTT also correlated the highest with traffic markers and transition metals ($r = 0.66 - 0.73$).

The relatively low spatial correlations between OP DTT and PM constituents suggest differences in OP sources between sites. The low measured values for OP DTT in our study may also have contributed to the low correlation with other components.

We can conclude that monitoring of standard pollutants (PM mass, NO₂) or elements will not fully capture the contrast of the evaluated organic pollutants (OC, PAH, levoglucosan) and OP.

1.3.4 Organic pollutants' monitoring cost and practicability

Decisions about any extension of air pollution monitoring through the addition of new pollutants must be also based on cost and practicability of the measurements. The relatively easy methods for the determinations of PM_{2.5} and PM₁₀ mass use a gravimetric approach for PM mass quantification. This method is described in the norm: EN 12341:2014, Ambient air - Standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter (CEN 2014b). However, most countries use more labour efficient, continuous monitors (e.g. TEOM or B-gauge monitors) for PM mass monitoring. The equivalency to standard method for PM measurement is tested according to an European norm: CEN/TS 16450:2013, Ambient air - Automated measuring systems for the measurement of the concentration of particulate matter (PM₁₀; PM_{2.5}) (CEN 2013).

In comparison a disadvantage of large scale **PAH** monitoring are high costs and time consuming analytical methods. The price of PAH analysis might be as high as 200 euro per sample in The Netherlands. Therefore there are fewer sites where PAH's are measured compared to PM₁₀. The European standard (CEN/TS 16645:2014: Ambient air - Method for the measurement of benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene) (CEN 2014a) describes a measurement method which comprises sampling of the selected PAH compounds as part of the PM₁₀ fraction, sample extraction and analysis by high performance liquid chromatography (HPLC) with fluorescence detector (FLD) or by gas chromatography with mass spectrometric detection (GC-MS).

Since the beginning of the 1980's the photoelectric aerosol sensors (PAS) have been known as tools for real time PAH monitoring. However, the monitors provide

semiquantitative profiles of particle related PAH (Childers et al. 2000) and therefore cannot be used as equivalent method standard method for PAH monitoring. The development of online, cheaper methods, which could be applied in compliance with CEN/TS 16645:2014) would lower the cost of PAH measurement. As a result the extension of PAH monitoring network would become more feasible.

The **levoglucosan** analytical method is slightly cheaper than PAH analysis (about 150 euro per sample in The Netherlands). Moreover, mostly high levels of levoglucosan in relation to analytical detection limit are found in ambient air which makes it easy to quantify. It is possible to use the same loaded filter that is used for other analyses such as EC and OC measurements. Mostly, levoglucosan is measured with with gas chromatography in combination with a mass spectrometric detection method. However, as there is no European standard analytical method for levoglucosan, there is a need to compare other existing analytical methods that are in use across Europe for the determination of levels of levoglucosan in air.

Wide scale monitoring of the ambient air concentrations of various **elements** involved in air pollution is less costly (about 30 – 40 euro per sample) than measurements of organic compounds but differences in spatial trends between elements and organic pollutants show that monitoring of elements will not capture the contrast of organic pollutants and will not reflect the level of risk caused by exposure to organic pollutants. However, it will give insight into population exposure to elements and their sources.

EC and OC are determined by thermal-optical analysis in a multistep process. There are several different protocols within the thermal-optical method that are commonly used to measure EC and OC, which differ in their output by up to a factor of two (Cavalli et al. 2009), since distinguishing EC from OC is very difficult. Additionally, there are no reference materials available which would help to determine correct EC and OC concentrations. Recently, the European standardisation working group (CEN/TC264/WG 35) has chosen EUSAAR2 protocol as the standard method for EC and OC analytical method in Europe (Cavalli et al. 2009). The draft of the standard is under review at CENELEC Management Centre (CCMC). This will enable collection of comparable EC and OC results within Europe. The costs of EC and OC analyses are substantially lower than costs of organic pollutants (between 50 and 100 euro per sample in the Netherlands).

Oxidative potential assays are still under investigation. Mostly the OP measurements are expensive and time consuming (ESR assay is an exception). Moreover, little is known about between inter-laboratory variations for the different assays. The comparison reported by Yang et al. shows that there are substantial differences between laboratories in results of DTT assay for example (Yang et al. 2014). The high between laboratory variations requires development of

standardized procedures in terms of OP measurements in any routine monitoring network. More automated procedures for the OP DTT determination are ongoing.

1.3.5 Conclusions

After considering several aspects of air pollution monitoring I would recommend the inclusion of levoglucosan in the routine air quality monitoring network in Europe. The decision on additional continuous monitoring for new pollutants should ultimately be made on the basis of results from wide-scale epidemiological studies on adverse health effects caused by these pollutants. A comparison of the air pollutants that were studied is presented in Table 5. The growing evidence of adverse health effects of wood smoke on human health is a strong argument to monitor exposure of the population to this source's emissions. Levoglucosan is the most credible and specific marker of woodsmoke combustion and is relatively easy to measure. Costs are lower than for PAH analyses. Its routine monitoring would help to evaluate (trends in) air quality impacts originating from wood combustion that is used for example for domestic heating or recreation.

The routine monitoring of other markers, presented in this thesis, meets several challenges. For **OP** there is currently insufficient evidence that it predicts health effects better than PM mass; the standardization of methods is insufficient and costs for assays such as the DTT assay are high. A problem for **PAH** is the expensive and laborious analytical method for PAH measurement. PAH are already measured and it is beyond the scope of this thesis to evaluate whether additional monitoring is needed. **OC** is also measured already along with EC. A disadvantage of OC is that it represents a highly variable class of organic components. It is unclear whether its measurement represents a step forward compared to already measured PM mass. Therefore I would recommend to wait until those issues are resolved before making decision concerning extension of routine air quality monitoring of already measured pollutants (PAH or OC) or inclusion of new markers as OP.

Table 5. Comparison of the individual air pollutants for inclusion in routine monitoring

	OC	PAH	OP	Levoglucosan
Specificity ¹	-	-	-	++
Spatial variation of annual averages ²	+	+	-	+
Cost/practicability	+	-	--*	+/-
Correlation with other pollutants ³	+	+	++	+
Health ⁴	+	++	-	++

¹ + = component and/or source specific marker

² + = high spatial contrasts of the annual concentrations

³ + = low correlation

⁴ + = evidence of adverse health effects

*Price depends on the type of OP assay

Taking into account the measured spatial variability of levoglucosan in this study, multiple sites per study area are needed to fully characterize its distribution. Urban and rural background sites are needed. Because of the high costs per analysis, an option is to perform analysis on filters only once every six days, as in the monitoring network in the USA for gravimetric PM measurements. Another option is to focus the analyses on the winter season with possibly measurements at a few sites in the summer season (depending on the major source of wood burning, e.g forest fires are more common in the summer season). In the Netherlands, PM_{2.5} is routinely measured at a sizable number of sites using quartz filters. These filters could be used, hence no new sampling is needed.

2. Modelling of concentrations of PM components

Exposure assessments for epidemiological studies of long-term exposure to ambient air pollution are still a challenge. Two main current approaches for assessing intra-urban air pollution contrasts are land-use regression (LUR) models and dispersion models. Recent comparison studies show that traffic-related pollutants can be modelled effectively with both dispersion and land use regression models, because of availability of traffic intensity and/or road category and length data and available data on traffic emissions and sufficient knowledge on dispersion of traffic related air pollution (de Hoogh et al. 2014).

However there is a growing need to investigate health effects caused by PM constituents. This remains a challenge for both methods mainly due to incomplete information on ambient background concentrations of individual components and insufficient knowledge and identification of individual pollutant sources.

2.1 LUR models

LUR modelling uses multiple linear regression to analyse associations between measured pollutant concentrations at a limited number of monitoring sites (typically 40 – 80) and predictor variables such as traffic, land use and topography. LUR models have been shown to be a cost-effective method to explain the spatial variation in air pollution in a number of studies (Hoek et al. 2008).

The LUR method was first developed by Briggs et al. (Briggs et al. 1997) and uses least squares regression to combine monitored data with Geographic Information System (GIS)-based predictor data that reflects pollutant sources and is then used to build a prediction model that is applicable to non-measured locations such as residential addresses of participants of an epidemiological study. LUR modelling has been increasingly used in epidemiological studies because it can be easily implemented on the basis of purpose designed monitoring campaigns or routinely measured concentrations and appropriate geographic predictors of air pollution sources (Hoek et al. 2008). Most modelled pollutants are PM_{2.5}, PM₁₀ and

compounds strongly affected by traffic (NO_2 , PM absorbance and EC) (Beelen et al. 2013, Eeftens et al. 2012a).

Recently, a growing number of studies present LUR models for particle composition other than elemental or black carbon (Table 6).

Elemental composition

Four recent studies presented LUR model development for selected elements (de Hoogh et al. 2013, Wu et al. 2014, Ho et al. 2015). Three of these studies used the supervised stepwise regression approach used in the ESCAPE project (Beelen et al. 2013, Eeftens et al. 2012a). Eight elements were selected from the 48 measured elements. These reflected different major sources of potentially toxic components and were measured above detection limit (de Hoogh et al. 2013). The eight elements were Cu, Fe, Zn, Ni, V, S, K and Si. LUR models predicted some elements (Fe, Cu and Zn) being associated with traffic as a main source well with explained variances higher than 57%. Across study areas, the models explained less variation for the other five elements, for which traffic is not a dominant source. In individual study areas, good predictive models were developed, such as for Ni and V in areas with significant ports (a major source for these elements because of their emission in the crude oil combustion processes) (de Hoogh, 2013). The moderate explained variance of LUR models for the five non-traffic components was due to a combination of factors, including lack of contrast in pollutant concentration (e.g. V in non-port study areas and S in smaller study areas), availability of variables describing the pollutant's sources and the lack of explicit incorporation of secondary particle formation (for S).

Wu et al. presented LUR models for eight elements in $\text{PM}_{2.5}$ (Cu, Fe, K, Mn, Ni, Si, S and Zn in a large Asian city (Wu et al. 2014). Developed models for Ni, Si and Mn had high explained variance ($R^2 > 75\%$) due to an important source of those elements - a large gravel plant. The models contained additionally variables representing port, industry, traffic and population density.

Ho et al. additionally investigated the vertical distribution of $\text{PM}_{2.5}$ and a number of elements (Cu, Fe, K, Mn, Ni, S, Si, Zn, Ti). The floor level was identified as a significant predictor in the $\text{PM}_{2.5}$, Si, and Fe models. The authors estimated that the concentrations differed 5.6% and 11.0% between the highest and lowest floor level. The results suggest that vertically distributed measurements should be considered in future LUR studies in urban areas with high-rise buildings (Ho et al. 2015). Traffic and industry related variables were included in models for all elements. The highest explained variance was found for Cu and Mn with R^2 of 80 and 74%, respectively. S and Ni had the lowest R^2 (46 and 47%, respectively).

In the NPACT study, models for OC, EC, Si and S were developed (Vedal et al. 2013). Spatiotemporal models were built for six US metropolitan areas. The variables offered for model development included a number of specific sources in the neighbourhood of sampling sites (road length, coastline, commercial area,

railroad , airport, large port) and emissions of the following pollutants: PM_{2.5}, PM₁₀, CO, SO₂, NO_x. The highest cross validation R² was found for the traffic marker EC (average CV R² = 54%), followed by OC (CV R² = 43%). For Si and S models had similar average CV R² - 23 and 22%, respectively. Vedal et al used 10-fold cross-validation which splits the data from home-outdoor sites into 10 groups, fits 10 models, each time leaving one group out.

Wood smoke

Challenges to obtain specific GIS predictor data were also met during modelling of exposure to wood smoke. Recently several studies reported LUR models of markers of wood smoke exposure (de Hoogh et al. 2013, Su et al. 2008, Larson et al. 2007, Smargiassi et al. 2012, Jedynska et al. 2015). The studies measured different pollutants to represent wood smoke particles: potassium (de Hoogh, 2013), levoglucosan (Su, 2008; Jedynska, 2015) and PM_{2.5} or PM₁ (Larson, 2007; Smargiassi, 2012). All those studies reported moderate levels of explained variance (R²)- 57% in Seattle (Su et al. 2008), 64% in Vancouver (Larson et al. 2007), 40% for the global model in Montreal (Smargiassi et al. 2012), a median of 60% for four European study areas (Jedynska et al. 2015) and an average of 53% for 20 European study areas (de Hoogh et al. 2013). However, for a number of individual study areas the explained variance of the presented models for levoglucosan, K or PM₁ were high – up till 90% (de Hoogh et al. 2013, Jedynska et al. 2015, Smargiassi et al. 2012).

In the two European studies there were no specific variables representing woodsmoke emissions in the model development (Jedynska et al. 2015, de Hoogh et al. 2013). The variables which entered the models were unspecific e.g. population density or natural areas. Additionally several models developed for potassium included traffic related variables that represent other sources of potassium than woodsmoke (de Hoogh, 2013). In the levoglucosan models, traffic variables did not enter the model, illustrating the importance of measuring a specific marker of woodsmoke, if the goal is to characterise woodsmoke emissions. In the Seattle and Vancouver studies, information about the use of woodstove or houses with wood heating was available (Su et al. 2008, Larson et al. 2007). In the model with the highest R² for Vancouver (reported by Larson et al.) wood smoke source variables were not included. The R² of this model was 84%. In this model, variables describing population and its social economic status were included. The inclusion of socio-economic variables as a predictor variable in a LUR model is however not an attractive direction, as this may introduce confounding when such models are applied in epidemiological analyses. In the best model presented by Su et al. for Seattle, the wood-heating units variable as well as percentage of population in manufacturing trade were used. The difference with the Vancouver study (Larson, 2007) could be due to the measurement of a more specific marker

for woodsmoke (levoglucosan instead of PM_{2.5}) and possibly the quality of the predictor data.

In the Montreal study *a priori* regional background PM_{2.5}, chimney density, elevation and temporal components (wind speed, temperature) were included (Smargiassi et al. 2012).

In our study we attempted to improve LUR models of levoglucosan and making them more specific for woodsmoke by adding information on emissions of woodsmoke at a 7*7 km spatial scale in four study areas (Jedynska et al. 2015). For the large study areas in the Netherlands and Catalonia, 7*7 km is a relevant scale, but for Munich-Augsburg and especially Oslo, the scale was likely too coarse to explain variability in measured concentrations. Available emission data on woodsmoke emissions did not enter the model (Chapter 4). That was probably caused by the insufficient quality of data we used, either because of incomplete availability of emission sources or unsatisfactory spatial resolution of emission data leading to insufficient contrast between sites in the area of interest. This conclusion applies to the purpose of this study and may not apply in the use of these emission data in large scale assessments. The current study was not intended as a validation of the emission data.

The American and European woodsmoke studies differed in approaches in terms of monitoring campaigns. Three North-American studies were based on mobile monitoring performed in winter evening hours only and averaged over routes or neighbourhoods. In the two European studies that we performed, we modelled average concentrations at fixed monitoring sites over 14-day averaged samples of levoglucosan or potassium including both daytime and night-time (Jedynska et al. 2015, de Hoogh et al. 2013). 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 (Smargiassi et al. 2012). This may be a reasonable assumption for variation during a measurement day, but likely less so for variation between days.

OC and PAH

Another group of LUR models presented recently relate to organic pollutants with multiple sources such as PAH, OC and hopanes/steranes.

One PAH LUR model was previously reported for daily PAH concentrations in Fresno, California (Noth et al. 2011). The spatiotemporal model included length of highway in a 500m buffer, proximity to roads and neighbourhood use of gas for heating as spatial variables in addition to temporal weather data. The authors reported an index of agreement (which can range from 0 to 100%) of 67% suggesting overall a good fit of the PAH models.

In the NPACT study, cross-validation R² values for the spatial part of intra-urban

spatiotemporal models were lower for OC than for EC (0.56 versus 0.81 for the six cities combined) (Vedal et al. 2013).

Table 6. Overview of published LUR models for PM composition

PM component	Study area	Specific non-traffic predictor variables	R ² [%]	LOOCV R ² [%]	Reference
Elements in PM2.5 and PM10 Cu, Fe, K, Ni, S, Si, V, Zn	20 European study areas	Port, industry	Elements in PM2.5: 43 – 72 Cu, Fe: 72, 71 In PM10: 53 – 79 Cu, Fe: 79, 76	Elements in PM2.5: 34 – 65 Cu, Fe: 65, 65 In PM10 45 – 73 Cu, Fe: 73, 70	(de Hoogh et al. 2013)
Elements in PM2.5 Cu, Fe, K, Mn, Ni, S, Si, Zn.	Kaohsiung City, Taiwan	Gravel plant, port, industry.	40 – 83 Cu, Fe: 69, 82	16 – 73 Cu, Fe: 59, 67	(Wu et al. 2011)
Elements in PM2.5 Cu, Fe, K, Mn, Ni, S, Si, Zn, Ti	Taipei City, Taiwan	Floor level, port, industry	46 – 80 Cu, Fe: 60 – 80	31 – 70 Cu, Fe: 40 – 70	(Ho et al. 2015)
EC, OC, Si, S in PM2.5	6 metropolitan areas in US	Distance to the nearest source (e.g. airport, port, coastline, railroad)	-	9 – 78 ¹	(Vedal et al. 2013)
PAH	Fresno, CA, US	Temporal component (meteorological data), homes with gas heating fuel	-	67% ²	(Noth et al. 2011)
PAH	10 European study areas	-	31 – 93	8 – 89	(Jedynska et al. 2014a)
PM1 as proxy of wood smoke	Quebec, Canada	Meteorological data, chimney density	40 – 94	-	(Smargiassi et al. 2012)
Light scattering coefficient as proxy of woodsmoke	Vancouver, Canada	Woodstove use, Socioeconomic status	40 – 84	-	(Larson et al. 2007)
Levoglucosan as proxy of woodsmoke	Seattle, WA, US	Houses with wood heating, Socioeconomic status	22 - 57	-	(Su et al. 2008)
Levoglucosan as proxy of woodsmoke	4 European study areas	-	59 – 71	36 – 62	(Jedynska et al. 2015)
OP in PM10 (GSH)	London, U.K.	-	-	25 – 73 ³	(Yanosky et al. 2012)
OP in PM2.5 (ESR, DTT)	The Netherlands	-	DTT: 60 ESR: 67	DTT: 47 ESR: 60	(Yang et al. 2015)
OP in PM2.5 (DTT)	10 European study areas	-	19 - 73	6 - 59	(Jedynska et al. submitted)

¹ 10-fold cross-validation; ² Instead of R², index of agreement reported
LOOCV = leave one out cross validation

The model R^2 for PAH and OC was generally lower than for more traffic-related components such as EC in the current study (Chapter 3). Median R^2 was 67 and 51% for PAH and OC respectively versus 84% for EC. In most of our models for OC, PAH and hopanes/steranes, traffic variables were included. We did not have detailed information on wood burning and industrial emissions, which are also OC and PAH sources. Non-traffic sources were represented by a more general variable such as population density or industrial land use. The available industrial land use data does not include type of industry (e.g. steel and metal industry), which is one of the PAH sources. The limited number of monitoring sites in the direct neighbourhood of industry further contributed to the limited inclusion of industry in our models.

Moreover, LUR modelling has limitations in terms of predicting pollutants with a strong secondary particle component such as OC (Jedynska et al. 2014a). Land use regression models cannot represent atmospheric formation processes explicitly. Reported explained variance for OC was 59% (Jedynska et al. 2014a). This model includes only variables describing primary sources of those pollutants e.g. traffic or industry. LUR studies have used approaches such as geographical coordinates, indicators for region of the country and distance to large sources areas to account for differences in pollutants formed in the atmosphere.

Organic carbon has next to primary origins (e.g. combustion processes) also a secondary origin from gas to particle conversion of volatile organic compounds in the atmosphere. This occurs either as a result of the condensation of low vapour pressure volatile organics, when concentrations exceed saturation levels, or from physical or chemical adsorption of gaseous species on aerosol particle surfaces, a process that can happen in sub-saturation conditions (Castro et al. 1999). There is little information available on exact contribution of secondary OC to total OC mass in Europe. There are recent developments in terms of dispersion modelling to predict OC concentration including secondary sources. More information on that is presented in paragraph 2.2.

In summary, limitations of current LUR models for PM components are due to a combination of a lack of specific predictor variables in a GIS for most non-traffic sources such as industry, wood burning and shipping; the design of monitoring campaigns that may not capture specific non-traffic sources well; and, limited prediction of atmospheric formation processes. As a result, model performance may be moderate. Furthermore models be insufficiently specific to separate health effects of different components in epidemiological studies. Section 2.3 describes approaches to improve LUR models of individual PM components.

2.2 Dispersion models

Dispersion models (DM) use information on emissions, source characteristics, chemical and physical properties of the pollutants, topography, and meteorology to model the transport and transformation of gaseous or particulate pollutants through the atmosphere to predict for example, ground level concentrations of pollutants (Holmes and Morawska. 2006; Kukkonen et al.. 2012). DMs rely on dispersion theory (e.g. Gaussian plume equation) and are based on simulation of the physical and chemical processes of transport and atmospheric chemistry using emission data, meteorological conditions and topographical data.

Tao et al presented a spatial dispersion model for 16 Environmental Protection Agency priority PAH. in Tianjin, a fast growing Chinese city with a population of 9 million people (Tao et al. 2006). Developed models, with resolution of 2 x 2 km, included several sources of PAH (e.g. coal used for power generation, gasification, central heating, coke production). The modelled PAH concentrations were lower than measured concentrations (up to two orders of magnitude) due to missing sources included in the model.

Sanka et al. developed a dispersion model for PAH in Liberec in the Czech Republic. The city of approximately 100,000 inhabitants is situated in a basin bordered by two mountain ranges. The comparison of the predicted with measured monthly average concentrations showed large differences. Measured PAH concentrations were generally higher (up to factor 5) and more variable than those predicted by the dispersion model. The correlations between measured and modelled concentration for all year was low (-0.32 – 0.27) (Sáňka et al. 2014). However after exclusion of concentrations below detection limits the correlation was higher (-0.22 – 0.97). As in the Tao et al study, the modelled PAH concentrations were in general lower than measured PAH levels. Discrepancies between measured and modelled data were attributed to weaknesses in the dispersion model (too simple model to reflect complex meteorological conditions and represent all physicochemical pollutants' properties), uncertainties in quantification of the air concentrations (use of passive samplers) and the impact of local sources not included in the emission inventory. In this study elements of GIS data were used for model improvement, to process source and elevation input data, create a receptor grid and cartographically visualise model results. According to the authors, the incorporation of GIS in data pre-processing and characterisation of spatial source distribution improved the accuracy of model inputs by using data from GIS databases such as the CORINE Land Cover database (Büttner et al. 2004).

A number of European studies have recently applied the CHIMERE chemistry-transport model to predict concentrations of carbonaceous aerosol and heavy metals (González et al. 2012, Bessagnet et al. 2008, Vivanco et al. 2011). The CHIMERE model has been extensively applied in Europe before, for modelling of

more common pollutants (sulfate, nitrate and ammonium components) (Bessagnet et al. 2004). The model includes physical processes such as anthropogenic emissions, atmospheric transport, mixing and deposition.

Two European studies used the CHIMERE model to predict concentrations of Pb, Cd, As, Ni, Cu, Zn, Cr and Se in Spain and background locations in Europe (Vivanco et al. 2011, González et al. 2012). Both studies modelled daily and annual average pollutants' concentrations with a resolution of 20 km. For that purpose the authors modelled some non-reactive heavy metals, considering emission, transport, mixing and deposition processes. In contrast to modelling of carbonaceous aerosol, no chemistry was considered for any of the metals. Some model overestimation was found for Pb, Cd, Ni and Zn (depending on the site up to a factor 5). A slight underestimation was observed for Cu in two study areas. The best agreement with observations was found for As, Se and Cr. The authors identified several possible reasons for discrepancies between modelled and measured metals' concentrations: used emission data did not correspond with simulated year, lower spatial resolution of the emission data (50 km) than the modelled one (20 km) and insufficient knowledge of temporal trends of the modelled metals.

Ambient concentrations of sulphate, nitrate and ammonium components have been modelled in Europe for decades with EMEP models (Eliassen, Saltbones 1983, Berge, Jakobsen 1998, Jonson et al. 1998). The EMEP network has extensive experience and a major role in terms of modelling of those components in Europe.

As mentioned in section 2.1, it is challenging to model organic carbon concentrations due to its substantial fraction of secondary organic carbon. Bessagnet et al included in CHIMERE model isoprene (emitted by vegetation) chemistry, which has a strong impact on secondary organic aerosols (SOA) formation. The model was used to predict daily, regional SOA levels in Europe with spatial resolution of 30 km. The study suggests that isoprene chemistry makes a strong contribution to SOA concentrations in Europe and could explain the large underestimation of OC concentrations in southern Europe when this specific chemistry is not accounted for, which was the case in the previous attempt of modelling of OC with the EMEP model by Simpson et al. (Simpson et al. 2007).

Based on the mentioned studies on DM, the most important challenges of dispersion modelling of air pollutants with multiples sources are: incomplete information on emission of specific pollutants, limited resolution of the emission data, and complex chemistry behind pollutant formation (e.g. OC). The relative importance of these limitations differs per group of components.

2.3 Possible improvements in modelling of particle composition

In order to study health effects of different components of PM, models need to explain more variation of measured concentration and be more specific for the component of interest. Inclusion of very generic predictor variables (e.g. population

density) may improve LUR model performance, but may not result in models that separate different PM components. Similarly, for dispersion models simplifying assumptions such as fixed ratios between EC and PM mass emissions may also artificially increase correlations between components.

2.3.1 LUR models

There are several approaches to improve LUR model predictions of specific ambient pollutants concentrations:

- a. Determination of variables describing sources of specific air pollutants
- b. Including more sites near sources other than traffic in measurement campaigns
- c. Inclusion of measured regional background concentration of the component of interest in the model
- d. Use of specific emission data as predictors
- e. Development of large scale, multi-city models
- f. General improvement of LUR models (more sites, fewer predictors)

These approaches can be distinguished into those potentially improving the specificity of the models (items a – d especially) and those that may improve LUR models performance in general (items e and f).

a. Determination of variables describing specific air pollution sources

In section 2.1 we identified that a major limitation of the land use regression modelling of air pollutants with other sources than motorised traffic is lack of variables representing those sources. This applied to most of the organic components modelled in this research. Most of the relatively readily available variables represented source strength of or proximity to traffic. Other sources were described by mostly unspecific variables such as population density and % natural/green areas in buffers surrounding the monitoring locations.

Additional determination of GIS variables describing other sources than traffic may be useful and feasible for industrial sources and wood smoke. by identifying those emission sources in the neighbourhood of the sampling sites. Repetition of LUR model development with an extended set of variables using existing measurement data may give an opportunity to improve the presented models. It may, however, be a substantial amount of work to obtain predictor variables beyond readily available land use and traffic data. For industrial sources, inclusion of type of

industry would be a step forward compared to the crude category of industrial land use used in the current study and most previous studies. To our knowledge no such database exists within the Netherlands, however knowledge about type of industry in the Netherlands is available in organisations developing emission registrations and authorities responsible for issuing permits. In a study in the Rijnmond area of the Netherlands, the LUR model including a non-specific industry variable, over-predicted NO₂ concentration in areas with light industry, illustrating the need for including type of industry (Beelen et al. 2010).

Inclusion of the location of major point sources could provide further improvements. An Asian study has recently reported a successful development of LUR models for PM elemental composition (Wu et al. 2014). LUR models for Ni, Si and Mn explained a high % of concentration variance (> 75%) due to an identification of significant point source of those elements in the study area – a major gravel plant. Particularly for point sources, dispersion models may, however, be superior because emission height and wind direction need to be taken into account in modelling concentration, much more so than for traffic emissions that are released at low height. Wind direction can be taken into account in LUR models through wind roses (Abernethy et al. 2013) or wind fields (Arain et al. 2007) as alternatives to traditional circular buffers. Improvement of data on emission of wood smoke may be difficult as in the Netherlands there is no database of private wood heaters. Special surveys may be needed to identify neighbourhoods with a large number of wood stoves. Given the importance of the source due to growing evidence of its adverse effect of human health and the annoyance related to wood smoke, such a survey may be very useful. Three North American studies which reported LUR models for prediction of wood smoke concentration used data on sources of wood smoke emission: chimney density or use of wood stoves (Smargiassi et al. 2012, Larson et al. 2007, Su et al. 2008). The variables describing wood smoke sources did not always enter the best predictive models. This is likely due to the relatively poor quality of the wood stove data (based on telephone survey data) and indicates that careful evaluation of the added value of new, specific predictor variables is needed. Improvement of data on shipping emissions could be achieved by including type of waterway to the land use variable used in the current study as air quality of several study areas included in the current study are influenced by water transport emissions. Data on the amount of ships per day is available for the larger waterways and within municipalities to some extent for urban waterways.

b. Study design including more sites influenced by specific sources

The ESCAPE study overrepresented traffic locations in the monitoring campaign, based on the assessment that motorised traffic was an important source of spatial concentration variations in all study areas. With 20 PM sites overall per study area, there were few possibilities to assess other sources specifically. Sites did differ in other characteristics such as population density, distance to city centre and

possibly other local conditions. Designing a new measurement campaign in order to develop LUR models requires inclusion of sites influenced by identified air pollution sources other than traffic (industry, shipping, wood smoke etc.). This will only be possible with an increase of the number of monitoring sites. This approach was applied in two American studies (Larson et al. 2007, Su et al. 2008) where measurement sites were chosen according to expected wood smoke emissions in order to model wood smoke concentrations. In the Larson study, mobile monitoring was performed to measure a large number of locations, focusing on season (winter) and time of day (evening/night) with the largest source strength. Currently, mobile monitoring allows determination of a limited number of air pollutants (e.g. PM_{2.5}, UFP or BC), because of lack of instruments for online monitoring of PM composition.

c. Inclusion of measured regional background concentration

Characterisation of the regional background concentration is important for larger study areas. Often, the variation of regional background is not well characterised by the GIS variables available for modelling, because the regional background may result from large scale processes of emission and potentially atmospheric formation. For NO₂ and PM_{2.5}, monitoring data from satellites provide a promising new option to characterise the regional background (Vienneau et al. 2013). Currently, no satellite data on PM composition is available. Interpolation of measured concentrations at regional background sites of specific monitoring campaigns can be used for PM composition. In a study at 40 ESCAPE sites across the Netherlands, interpolated regional background concentration of oxidative potential (OP) was included in a LUR model for OP (Yang et al. 2015). This increased the specificity of the OP model compared to models for other components developed on the same sites.

d. Use of emission, meteorological data as additional variables

Another approach to improve LUR models is inclusion of information primarily used in DMs e.g. meteorological and emission data. In the currently reported study (chapter 4), for development of LUR model for levoglucosan, the European wood smoke emission data was used in addition to GIS predictor variables that were unspecific for wood smoke emissions (chapter 4). Emission data of PM_{2.5}, EC, OC, and B[a]P originating from wood smoke were 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.gmesatmosphere.eu/>) and TRANSPHORM (www.transphorm.eu). The data was available for grids of 7 × 7 km for all four study areas and additionally in The Netherlands in the grid of 1 × 1 km. The emission data did not enter the final model. That indicates that the quality, especially spatial resolution, of emission data is of great importance while considered in LUR development. Previous studies that

evaluated emissions as a predictor for NO₂ LUR models also found that they did not improve LUR models based upon traffic and population data (Hoek et al, 2008). This was attributed to the relatively poor spatial resolution.

e. Developing large scale, multi- city LUR models.

Recently a number of studies reported large-scale LUR models for PM, NO₂ and soot. The studies were performed in North America and Europe (Novotny et al. 2011, Wang et al. 2014, Vienneau et al. 2013). The development of large-scale LUR models allows the prediction of the component concentrations in areas where no measurements are taken. Further, for specific study areas with poor model predictions the large-scale model can provide improved prediction of pollutant concentrations. The model offers the possibility for pooled epidemiological analyses in addition to local cohort studies (Wang et al. 2014). Multi city models allow also the inclusion of new study populations from areas where local measurements were never conducted but relevant predictor variables are available. The development of large-scale models is based upon a larger number of monitoring sites than local LUR models. Recent studies have documented that the ability of models to predict variability of external monitoring data increases substantially with increasing number of monitoring sites used for model building (Wang, 2012; Basagana, 2012; Wang, 2013).

To my knowledge only one study published studies presenting wide scale models for specific PM components (Vedal et al. 2013). Vedal et al presented combined models for six American for: Si, SO₄, OC, EC. All models explained high level of variance ($R^2 = 72\% - 92\%$).

In Chapter 5 I presented a European model for oxidative potential determined with the DTT assay. The model R^2 was only 30%, but the model was more robust in comparison to most of the models for individual study areas. Only for five out of ten study areas, a LUR model could be developed. From these five models, only two had a R^2 higher than 50% and the median R^2 of the five models was only 33%. Our European DTT model included more specific variables (distance to port, population density) instead of green area or altitude (in Paris) in individual models. Distance to port was also found to be a significant source of DTT in an American study (Hu et al. 2008). Moreover the model was more robust with only 4% R^2 drop after leave one out cross validation (Wang et al. 2013b) while the median R^2 decrease of the five individual models was 11%. The large-scale LUR model allows estimation of pollutant concentration in the study areas where individual models could not be built.

f. General improvement of LUR models

Based on the observed over-fitting of models (Wang et al. 2013a, Wang et al. 2012, Basagaña et al. 2012), a few recommendations can be made that apply to all LUR modelling studies. This includes:

1. More monitoring sites, even at the expense of shorter monitoring time per site
2. Fewer predictor variables e.g. by restricting the number of buffer sizes for models based on limited number of sites, such that the ratio between number of predictors and number of sites is not too large (Basagana et al. 2013)
3. Accepting only functional relationships that are based upon theory (e.g. exponential distance to road decay which is based on observations that air pollutants' concentrations decrease exponentially with increasing distance from the road).
4. Inclusion of street configuration. Eeftens et al has recently investigated the impact of inclusion of street configuration indicators on LUR model performance (Eeftens et al. 2013). Despite the small increase in R^2 (2% for NO_x and NO_2 models), contrasts in "SkyView Factor" (SVF), a measure of the total fraction of visible sky, (10th - 90th percentile) resulted in substantial concentration differences of $5.56 \mu\text{g}/\text{m}^3$ in NO_2 and $10.9 \mu\text{g}/\text{m}^3$ in NO_x .
5. Inclusion of vertical distribution. The vertical distribution of $\text{PM}_{2.5}$ and a number of elements (Cu, Fe, K, Mn, Ni, S, Si, Zn, Ti) was investigated by Ho et al. (Ho et al. 2015) The floor level was identified as a significant predictor in the $\text{PM}_{2.5}$, Si, and Fe models.

2.3.2 Dispersion models

Prediction of concentrations of pollutants with multiple sources with dispersion models requires further improvement of the data bases used with this technique. The essential developments of DM method are: development of knowledge of the temporal behaviour of specific pollutant emissions, improvement of the accuracy and spatial resolution of the emission data used in the model development, identification and inclusion of all sources contributing to specific pollutant emissions, development of extensive knowledge of transport and dispersion processes of the PM components, incorporation of chemistry affecting a pollutant concentration, employing spatial tools like geographic information system (GIS) which may help in processing of input data as well as visualisation of the modelling results.

To improve dispersion modelling of OC concentrations the development of knowledge regarding sources and modelling of secondary OC is necessary. Further understanding the primary and secondary OC contribution in total OC in the studied area must be considered. Bessagnet et al included in the CHIMERE model isoprene chemistry, a significant biogenic source of secondary OC (Bessagnet et al. 2008).

With regards to improvement of dispersion models for metal concentrations, the following issues should be considered: improved characterisation of emission sources, both with respect to the magnitude and the location of emissions; more recent annual total emissions, information on SNAP activities for each metal, higher spatial resolution and a better knowledge of the temporal emission behaviour is necessary to adequately model these air pollutants. Also extended knowledge of metal size distribution, deposition and chemical processes could result in better model results (González et al. 2012).

As for metals, the improvement of DM for PAH concentrations requires further improvement of the knowledge on PAH sources (identification and contribution to total emissions). The examples of sources not included in the published DM models but identified by authors were: incidental PAH sources e.g. biomass burning, open-fire cooking and also various secondary pollution sources, including releases from historically contaminated areas (e.g. soil-to-air diffusion) (Sáňka et al. 2014, Tao et al. 2006). Further, knowledge of chemical transformations of organic pollutants and their atmospheric scavenging will help with the improvement of dispersion models.

Finally, an increased number of monitoring stations and a better temporal coverage of observations are also important to carry out a better statistical analysis of dispersion models and their performance and to plan and apply future models improvements.

2.3.3 Beyond LUR and dispersion modelling

The first development that may contribute to better and more specific modelling of particle composition is combination of dispersion and LUR modelling in one model, so-called hybrid models. Hybrid models have been shown to improve upon the individual models for NO₂ (Wilton et al. 2010). Hybrid models may be particularly interesting for components with important primary emissions and secondary atmospheric formation, such as OC.

A second option is to rely more on the actual measurements of components to assign exposures to individual subjects of an epidemiological study. Exposure can be assigned using methods such as nearest station in neighbourhood, average of stations in the city of residence or interpolation of measurements. These methods have been applied in earlier epidemiological studies, exploiting especially between-city contrasts in exposure such as in the ACS study (Pope III et al. 2002), and in a

cohort study in California on particle components (Ostro et al. 2011). If sufficient contrast in concentration between cities exists relative to the within-city contrasts, this method may be feasible. For studies investigating health effects of different components of PM, it avoids the difficult modelling step that may not result in sufficiently specific models to disentangle health effect of different components.

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Summary

Summary

Summary

It has been shown that human exposure to air pollution causes adverse health effects. The most used indicator of air quality is the concentration of particulate matter with diameters smaller than 2.5 or 10 μm (PM_{2.5}, PM₁₀, respectively). However, PM is a chemically complex mixture and it has been suggested that observed adverse health effects depend on PM chemical composition. Most studies of PM composition have investigated short term health effects caused. In Europe, recently the ESCAPE project contributed significantly to development of knowledge on long term adverse health effect of PM elemental constituents. But still there is little knowledge about long term adverse health effects caused by exposure to organic PM components.

This thesis work contributes new insights into characterization of air quality by monitoring and modelling of specific organic components and oxidative potential. The goals of the thesis were:

- Determination of the spatial contrast of the ambient concentration of specific organic components (EC/OC, PAH and hopanes/steranes, levoglucosan) and oxidative potential within and between European study areas.
- Assessment of the relationship between those components with other components measured within the ESCAPE project (NO₂, NO_x, PM_{2.5} mass and absorbance).
- Development and evaluation of LUR models for EC, OC, PAH and hopanes/steranes, levoglucosan and oxidative potential.
- Assessment of the correlation of the predictions of the developed models with the predictions of the earlier published models for PM_{2.5} and PM_{2.5} absorbance.

The thesis was developed in the framework of the ESCAPE and THTRANSFORM projects. ESCAPE (European Study of Cohorts for Air Pollution Effects) and TRANSFORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) are EU FP7 funded projects designed to provide advanced knowledge on the impact of transport emissions and outdoor air pollution on human health in Europe. In the framework of the ESCAPE project, 36 study areas spread across Europe were used to assess concentrations of NO_x and NO₂ across Europe. In 20 of those study areas PM_{2.5}, PM₁₀, PM_{2.5} absorbance and elemental composition were measured. We added measurement and modelling of specific organic components and oxidative potential of PM_{2.5} in 10 study areas where PM mass was measured. The study areas included in this thesis were: Oslo, Helsinki/Turku, Copenhagen, London / Oxford, Netherlands, Paris, Munich/Augsburg, Catalonia, Rome and Athens.

In **Chapter 2**, the spatial variation of EC/OC, PAH and hopanes/steranes between and within 10 European study areas is presented. The spatial relationship between

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those components and the more frequently measured NO_x , NO_2 , $\text{PM}_{2.5}$ mass and absorbance was assessed. Substantial variability was found in spatial patterns of EC, OC, PAH and hopanes/steranes. EC and OC concentrations had similar patterns in Europe as the previously reported components NO_x , $\text{PM}_{2.5}$ and PM absorbance. The highest concentrations for those pollutants were found in southern Europe. The highest average EC and OC concentrations were found in Rome, where levels were 2.3 and 3.7 $\mu\text{g}/\text{m}^3$, respectively. In Oslo, EC and OC concentrations were lowest at 0.8 and 1.1 $\mu\text{g}/\text{m}^3$, respectively. ΣPAH exhibited a different trend in Europe. In southern and northern Europe, concentrations of those pollutants were similar with the highest concentrations in Copenhagen (2.1 ng/m^3), Rome and Athens (both 2.0 ng/m^3).

Linear regression method in combination with information from geographic information system about traffic, population density and land use around the sampling sites was used to explain measured spatial variation of PM constituents. The developed LUR models for EC/OC and PAH for each of the ten study areas and hopanes and steranes in four areas and their evaluation are presented in **Chapter 3**. The highest median explained variance (R^2) of the ten models was found for EC – 84%. The median model R^2 for OC was 51%, for benzo[a]pyrene, 67% and for the sum of hopanes/steranes, 38%. Traffic predictors were included in most models. The correlation of predictions from these PM composition LUR models with predicted $\text{PM}_{2.5}$ and $\text{PM}_{2.5}$ absorbance was on average moderate but varied substantially between study areas. The median correlation between predictions of $\text{PM}_{2.5}$ models and OC and ΣPAH models was 0.47 and 0.52, respectively, suggesting that the new models provide new air pollution characterization.

In **Chapter 4** the spatial variation of the wood smoke marker levoglucosan between and within four study areas (Oslo in Norway, The Netherlands, the Munich/Augsburg region of Germany and Catalonia in Spain) is presented. Levoglucosan concentrations were highest in Munich/Augsburg (102 ng/m^3) and lowest in Catalonia (64 ng/m^3), although the differences were not statistically significant. The contribution of wood-smoke, calculated on the basis of levoglucosan measurements and previous European emission data to OC and $\text{PM}_{2.5}$ mass was 13 to 28% and 3 to 9% per study area respectively over the full year studied. Larger contributions were calculated for the cold period. Across all areas, the highest within-study area correlation of levoglucosan was found with ΣPAH and B[a]P with median correlation coefficients of 0.65 and 0.58, respectively. The lowest correlation was found between levoglucosan and traffic markers: $\Sigma\text{hopanes/steranes}$ and NO_x (median $r = -0.22$). A relatively poor correlation was found between potassium in $\text{PM}_{2.5}$ (another marker for wood smoke) and levoglucosan (median $r = 0.33$). Finally, LUR models of levoglucosan for the four study areas were developed. All models had a reasonably high R^2 . The lowest R^2 was found in Oslo ($R^2 = 0.59$) and the highest in Catalonia ($R^2 = 0.71$). Variables

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used in our models were unspecific for wood combustion emissions, but were variables associated with general human activity.

In **Chapter 5** the spatial variation of oxidative potential measured with the DTT assay between and within ten European study areas is presented. Significant spatial contrasts were found for OP DTT between the study areas. The lowest OP DTT level were found in London and two Nordic areas – Oslo and Helsinki/Turku (0.14, 0.13 and 0.14 nmolDTT/min*m³ respectively). The highest OP levels were found in southern Europe. The difference between South and North-European areas was however smaller than observed for PM_{2.5}, NO₂ and PM_{2.5} absorbance. At street sites slightly higher OP DTT values were found compared to urban background sites (median ratio 1.10). The street/background was (much) smaller than for PM_{2.5}, NO₂ and PM_{2.5} absorbance. The small ratio suggests that the OP DTT assay will not be very useful in characterizing exposure for the roadway proximity studies. LUR models could only be developed for OP DTT for five out of ten study areas. A relatively low explained variance (median R² = 33%) was found for the five areas. A European level model combining all ten study areas resulted in a model R² of 30%, which was more robust than the study-area specific models. The model included residential density, port and traffic variables. Overall, LUR models did not effectively model spatial variation of OP DTT.

Chapter 6 consists of discussion of the main findings of this thesis, including potential implications for routine monitoring networks and modeling of PM composition and recommended improvement for future modeling studies. The first part of the discussion focuses on current European air quality monitoring legislation, design of current air quality monitoring network in Europe and supersites. Further, an answer for a question: Should European air quality monitoring be expanded? is discussed by analysing the following aspects of particle components: health effects of PM composition; spatial and temporal variation of PM organic pollutants; specificity of individual air pollution markers (OC, OP, PAH, levoglucosan) and their correlation with PM mass and elements; monitoring cost and practicability. My conclusion is that adding levoglucosan to routine monitoring would be useful.

In the second part of the discussion, the successes and limitations of PM composition modelling are reviewed. Land use regression models of PM composition, dispersion modelling of PM components, presented in recent literature, are discussed. Finally, possible improvements of modelling of specific PM components by LUR and dispersion models are suggested and discussed. There is a need to improve the specificity of the LUR models, by collecting more specific GIS predictors and more focused monitoring campaigns.

Samenvatting

Samenvatting

Het is bekend dat blootstelling van mensen aan luchtverontreiniging nadelige effecten op de gezondheid veroorzaakt. De meest gebruikte indicator van de luchtkwaliteit is de concentratie van fijn stof met een diameter kleiner dan 2.5 of 10 micrometer (PM2.5, PM10 respectievelijk). Echter, fijn stof is een chemisch complex mengsel. Er zijn aanwijzingen dat de waargenomen nadelige gezondheidseffecten afhankelijk zijn van de chemische samenstelling van het stof. De meeste studies hebben de gezondheidseffecten van korte termijn blootstelling aan stofcomponenten onderzocht. Het European Study of Cohorts for Air Pollution Effects (ESCAPE) project heeft recent een belangrijke bijdrage aan de ontwikkeling van kennis over gezondheidseffecten van lange termijn blootstelling van de elementaire samenstelling van stof geleverd. Er is weinig kennis over de gezondheidseffecten van lange termijn blootstelling aan organische stof componenten.

Dit proefschrift draagt bij aan nieuwe inzichten in de karakterisering van de luchtkwaliteit door monitoring en modellering van specifieke organische componenten en oxidatieve potentieel. De doelstellingen van dit proefschrift waren:

- Bepaling van het ruimtelijke contrast van de buitenlucht concentratie van specifieke organische componenten (EC / OC, PAK en hopanen / steranen, levoglucosan) en oxidatieve potentieel binnen en tussen Europese studie gebieden.
- Bepaling van de relatie tussen de concentratie van deze componenten en andere componenten gemeten binnen het ESCAPE-project (NO₂, NO_x, PM2.5 massa en absorptie).
- Ontwikkeling en evaluatie van land use regressie modellen voor de ruimtelijke variatie van EC, OC, PAK en hopanen/steranen, levoglucosan en oxidatieve potentieel.
- Evaluatie van de correlatie van de voorspellingen van de ontwikkelde modellen met de voorspellingen van de eerder gepubliceerde modellen voor PM2.5 en PM2.5 absorptie.

Het proefschrift werd ontwikkeld in het kader van de ESCAPE en TRANSPHORM projecten. ESCAPE en TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter) zijn door het EU FP7 programma gefinancierde projecten ontworpen om geavanceerde kennis te leveren over de gevolgen van de emissies van de transport sector en buitenluchtverontreiniging in het algemeen voor de gezondheid van de mens in Europa. In het kader van het ESCAPE project werden in 36 studiegebieden verspreid over Europa concentraties van NO_x en NO₂ gemeten en gemodelleerd. In 20 van die studiegebieden zijn ook PM2.5, PM10, PM2.5 absorptie en elementaire samenstelling gemeten en gemodelleerd. Voor dit proefschrift voegden we metingen en modelleren van specifieke organische componenten en oxidatieve

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potentieel van PM_{2.5} toe in 10 van de gebieden met stofmetingen. De onderzochte studiegebieden waren Oslo, Helsinki/Turku, Kopenhagen, Londen / Oxford, Nederland, Parijs, Munchen/Augsburg, Catalonie, Rome en Athene.

In **hoofdstuk 2** wordt de ruimtelijke variatie van de concentratie EC / OC, PAK en hopanen/steranen tussen en binnen de 10 Europese studie gebieden gepresenteerd. De ruimtelijke relatie tussen deze componenten en vaker gemeten NO_x, NO₂, PM_{2.5} massa en absorptie werd berekend. Aanzienlijke verschillen zijn gevonden in de ruimtelijke patronen van EC, OC, PAK en hopanen / steranen. EC en OC concentraties hadden vergelijkbare patronen in Europa als de eerder gerapporteerde componenten NO_x, PM_{2.5} en PM absorptie. De hoogste concentraties van deze verontreinigende stoffen zijn gevonden in Zuid-Europa. De hoogste gemiddelde EC en OC concentraties zijn gemeten in Rome: 2.3 en 3.7 µg/m³, respectievelijk. In Oslo, waren EC en OC concentraties het laagst: 0.8 en 1.1 µg/m³, respectievelijk. Som van de PAK's vertoonde een andere trend in Europa. In Zuid- en Noord-Europa, waren de concentraties van de verontreinigende stoffen vergelijkbaar. De hoogste concentraties zijn in Kopenhagen (2.1 ng/m³), Rome en Athene (beide 2.0 ng/m³) gemeten

Met behulp van informatie uit geografische informatiesystemen over verkeer, bevolkingsdichtheid en landgebruik rond de meetpunten is met lineaire regressie geprobeerd om de gemeten ruimtelijke variatie te verklaren. De ontwikkelde land use regressie (LUR) modellen voor EC / OC en PAK voor elk van de tien studiegebieden en hopanen en steranen in vier gebieden en de evaluatie van deze modellen wordt gepresenteerd in **hoofdstuk 3**. De hoogste mediaan van de verklaarde variantie (R²) van de tien modellen werd gevonden voor EC - 84%. De mediane model R² voor OC was 51%, voor benzo[a]pyreen, 67% en voor de som van hopanen/steranen, 38%. Verkeergelateerde variabelen werden opgenomen in de meeste modellen. De correlatie van de voorspellingen van deze PM samenstelling LUR modellen met voorspelde PM_{2.5} en PM_{2.5} absorptie was gemiddeld matig, maar aanzienlijk varieerde tussen studiegebieden. De mediane correlatie tussen de voorspellingen van OC en ΣPAH modellen en PM_{2.5} modellen en was 0,47 en 0,52 respectievelijk, wat suggereert dat de nieuwe modellen nieuwe karakterisering van luchtkwaliteit geven.

In **hoofdstuk 4**, wordt de ruimtelijke variatie van de hout rook marker levoglucosan tussen en binnen vier studiegebieden (Oslo in Noorwegen, Nederland, München / Augsburg gebied in Duitsland en Catalonië in Spanje) gepresenteerd. Levoglucosan concentraties waren het hoogst in München / Augsburg (102 ng/m³) en het laagst in Catalonië (64 ng/m³), hoewel de verschillen tussen de gebieden niet statistisch significant waren. De bijdrage van hout-rook, berekend op basis van levoglucosan metingen en eerdere Europese emissiegegevens aan OC en PM_{2.5} massa was 13-28% en 3-9% per studiegebied respectievelijk over het hele jaar.

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Grotere bijdragen werden berekend voor de winter periode. Binnen studiegebieden werd de hoogste correlatie van levoglucosan gevonden met Σ PAH en B[a]P met mediane correlatiecoëfficiënten van 0,65 en 0,58 respectievelijk. De laagste correlatie werd gevonden tussen levoglucosan en verkeer markers: Σ hopanen / steranen en NO_x (mediaan $r = -0.22$). Een relatief lage correlatie werd ook gevonden tussen kalium in $\text{PM}_{2.5}$ (een andere marker voor hout rook) en levoglucosan (mediaan $r = 0.33$). Tenslotte zijn LUR modellen van levoglucosan voor de vier studiegebieden ontwikkeld. Alle modellen hebben een redelijk hoge R^2 . De laagste R^2 werd gevonden in Oslo ($R^2 = 0.59$) en de hoogste in Catalonië ($R^2 = 0.71$). Variabelen gebruikt in onze modellen waren niet specifiek voor houtverbranding uitstoot, maar waren gerelateerd aan algemene menselijke activiteit.

In **hoofdstuk 5**, wordt de ruimtelijke variatie van oxidatieve potentieel gemeten met de DTT-test tussen en binnen tien Europese studiegebieden wordt gepresenteerd. Significante ruimtelijke contrasten waren gevonden voor OP DTT tussen de studiegebieden. De laagste OP DTT niveau werden gevonden in Londen en twee noordelijke gebieden - Oslo en Helsinki /Turku (0.14, 0.13 en 0.14 $\text{nmolDTT}/\text{min} \cdot \text{m}^3$ respectievelijk). De hoogste OP niveaus werden gevonden in Zuid-Europa. Het verschil tussen Zuid- en Noord-Europese gebieden was echter kleiner dan voor $\text{PM}_{2.5}$, NO_2 en $\text{PM}_{2.5}$ absorptie. Op straat locaties werden iets hoger OP DTT niveaus gevonden in vergelijking met stedelijke achtergrond sites (median ratio 1.10). De straat/achtergrond ratio was (veel) kleiner dan voor $\text{PM}_{2.5}$, NO_2 en $\text{PM}_{2.5}$ absorptie. De kleine verhouding tussen straat en achtergrond suggereert dat de OP DTT assay niet erg nuttig is bij het karakteriseren van de blootstelling in studies die specifiek lokale verkeergerelateerde luchtverontreiniging onderzoeken. LUR modellen konden alleen ontwikkeld worden voor vijf van de tien studiegebieden. Een relatief lage verklaarde variantie (median $R^2 = 33\%$) werd gevonden voor deze vijf gebieden. Een Europees model combineerde alle tien de studie gebieden en resulteerde in een model R^2 van 30%. Het Europese model was robuuster dan de modellen in de individuele studiegebieden. Het model bevatte variables gerelateerde aan adrestdichtheid, haven en verkeer. LUR modellen waren niet effectief in het modelleren van de ruimtelijke variatie van OP DTT.

Hoofdstuk 6 bestaat uit de discussie van de belangrijkste bevindingen van dit proefschrift, met inbegrip van mogelijke gevolgen voor de routine meetnetten voor luchtkwaliteit, modellering van de stof samenstelling en aanbevolen verbetering voor toekomstige modelleringsstudies. Het eerste deel van de discussie richt zich op de huidige Europese luchtkwaliteit wetgeving, het ontwerp van de huidige meetnetten van de luchtkwaliteit in Europa en supersites. De discussie geeft een antwoord op de vraag: Moeten Europese meetnetten van luchtkwaliteit worden uitgebreid? Dit wordt besproken door analyse van de volgende aspecten van

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deeltjescomponenten: gezondheidseffecten van stof componenten; ruimtelijke en temporele variatie van organische componenten van stof; specificiteit van individuele markers luchtvervuiling en hun correlatie met PM massa en elementen; kosten en uitvoerbaarheid. Mijn conclusie is dat het toevoegen van levoglucosan aan routinemonitoring nuttig zou zijn.

In het tweede deel van de discussie, worden de successen en beperkingen van het modelleren van de samenstelling van stof besproken. Land use regressie modellen van stof samenstelling, dispersie modellering van stofcomponenten worden besproken. Tot slot, worden mogelijke verbeteringen van de modellering van specifieke stof componenten door LUR en dispersie modellen besproken. Het is belangrijk om de specificiteit van de LUR modellen te verbeteren, door het verzamelen van meer specifieke GIS voorspellers en mogelijk meer gerichte meetcampagnes.

Affiliation of contributors

Helgah Akhlaghi Makarem

TNO, The Netherlands Applied Research Organization, Utrecht, The Netherlands

Christophe Ampe

AIRPARIF, Paris, France

Rob Beelen

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands
National Institute for Public Health and the Environment (RIVM), The Netherlands

Bert Brunekreef

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands
Julius Center for Health Sciences and Primary Care, University Medical Center
Utrecht, Utrecht, The Netherlands

Giulia Cesaroni

Epidemiology Department, Lazio Regional Health Service, Rome, Italy

Marta Cirach

Center for Research in Environmental Epidemiology (CREAL), Barcelona, Spain
IMIM (Hospital del Mar Research Institute), Barcelona, Spain
CIBER Epidemiología y Salud Pública (CIBERESP), Spain

Josef Cyrus

Helmholtz Centre for Environmental Research, Munich, Germany
University of Augsburg, Environmental Science Center, Augsburg, Germany

Kees de Hoogh

MRC-HPA Centre for Environment and Health, Department of Epidemiology and
Biostatistics, Imperial College London, London, United Kingdom
Swiss Tropical and Public Health Institute, Basel, Switzerland
University of Basel, Basel, Switzerland

Audrey De Nazelle

Center for Research in Environmental Epidemiology (CREAL), Barcelona, Spain
Centre for Environmental Policy, Imperial College London, UK

Christophe Declercq (deceased)

French Institute for Public Health Surveillance (InVS), Saint-Maurice Cedex,
France

Konstantina Dimakopoulou

Department of Hygiene, Epidemiology & Medical Statistics, Medical School,
National and Kapodistrian University of Athens, Greece

Affiliation of contributors

Marloes Eeftens

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands
Department of Epidemiology and Public Health, Swiss Tropical and Public Health
Institute, Basel, Switzerland
University of Basel, Basel, Switzerland

Kirsten T. Eriksen

Danish Cancer Society Research Center, Copenhagen, Denmark

Francesco Forastiere

Epidemiology Department, Lazio Regional Health Service, Rome, Italy

Gerard Hoek

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands

Nicole A.H. Janssen

National Institute for Public Health and the Environment (RIVM), The Netherlands

Klea Katsouyanni

Department of Hygiene, Epidemiology & Medical Statistics, Medical School,
National and Kapodistrian University of Athens, Greece

Menno Keuken

TNO, The Netherlands Applied Research Organization, Utrecht, The Netherlands

Ingeborg M. Kooter

TNO, The Netherlands Applied Research Organization, Utrecht, The Netherlands

Timo Lanki

Department of Environmental Health, National Institute for Health and Welfare
(THL), Kuopio, Finland

Christian Madsen

Division of Epidemiology, Norwegian Institute of Public Health, Oslo, Norway

Kees Meliefste

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands

Mark Nieuwenhuijsen

Center for Research in Environmental Epidemiology (CREAL), Barcelona, Spain
IMIM (Hospital del Mar Research Institute), Barcelona, Spain
CIBER Epidemiología y Salud Pública (CIBERESP), Spain

Wenche Nystad

Division of Epidemiology, Norwegian Institute of Public Health, Oslo, Norway

Marieke Oldenwening

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands

Affiliation of contributors

Arto Pennanen

Department of Environmental Health, National Institute for Health and Welfare (THL), Kuopio, Finland

Ole Raaschou-Nielsen

Danish Cancer Society Research Center, Copenhagen, Denmark

Morgane Stempfelet,

French Institute for Public Health Surveillance (InVS), Saint-Maurice Cedex, France

Antoon Visschedijk

TNO, The Netherlands Applied Research Organization, Utrecht, The Netherlands

Meng Wang

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands
Department of Environmental and Occupational Health Sciences, University of Washington, The United States

Aileen Yang

Institute for Risk Assessment Sciences, Utrecht University, The Netherlands
National Institute for Public Health and the Environment (RIVM), The Netherlands

Tarja Yli-Tuomi

Department of Environmental Health, National Institute for Health and Welfare (THL), Kuopio, Finland

Abbreviations

Abbreviations

B[a]P	benzo[a]pyrene
BC	black carbon
CO	carbon oxide
Cu	copper
CV	cross validation
DM	dispersion models
DTT	dithiothreitol
EC	elemental carbon
EMEP	The European Monitoring and Evaluation Programme
EPA	United States Environmental Protection Agency
ERS	electron spin resonanc
ESCAPE	European Study of Cohort for Air Pollution Effects
EU	European Union
Fe	iron
FLD	fluorescence detector
GC	gas chromatography
GIS	Geographic Information Systems
HPLC	high performance liquid chromatography
PAH	polycyclic aromatic hydrocarbons
K	potassium
LOOCV	leave-one-out cross validation
LUR	Land Use Regression
Mn	manganese
MS	mass spectrometry
NH₃	ammonia
Ni	nickel

Abbreviations

NO₂	nitrogen dioxide
NO_x	nitrogen oxides
OC	organic carbon
OP	oxidative potential
PM_{2.5}	mass concentration of particles less than 2.5 µm in size
PM₁₀	mass concentration of particles less than 10 µm in size;
PM_{2.5}abs	measurement of the blackness of PM _{2.5} filters, this is a proxy for elemental carbon, which is the dominant light absorbing substance
RB	regional background site
S	street site
S	sulfur
Si	silicon
SO₂	sulfur dioxide
SOA	secondary organic aerosol
RMSE	root-mean-square error
TRANSPHORM	Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter
Ti	titanium
UB	urban background site
V	vanadium
VOC	volatile organic compounds
WHO	World Health Organization
WMO	World Meteorological Organization
Zn	zinc

Abbreviations

Curriculum Vitae

Curriculum Vitae

Aleksandra Jedynska was born on 11th July, 1978 in Lodz, Poland. After graduating her high school in 1997, she started her study in environmental engineering in Lodz University of Technology. In 2001, within the Tempus Programme she participated in the student exchange with HZ University of Applied Sciences, Vlissingen, The Netherlands, where she obtained Bachelor Degree in Analytical Chemistry. Back in Poland, in 2004 she completed her MSc program with a thesis in waste management. After that, she worked for two years at SGS Environmental Services in The Netherlands.

Next, she travelled for one year in Asia and New Zealand, where, as a volunteer, she participated in several nature conservation projects in New Zealand Department of Conservation. After returning to The Netherlands, she worked as researcher at the Unilever Research and Development Center on development of new food products. Since 2007, she has been working at TNO, The Netherlands Applied Research Organization, in the group Applied Environmental Chemistry. She has been mainly involved in characterization of air pollution including activities such as: development and implementation of analytical methods (e.g. elementary and organic carbon, oxidative potential) and project management.

She is a member of the European standardization working group collaborating on development of European standard analytical method for determination of elementary and organic carbon in ambient particulate matter. In 2009 she started working on her PhD research project in cooperation with the Institute for Risk Assessment Sciences (IRAS) of Utrecht University (The Netherlands).

Her PhD research is conducted within 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). The focus of her PhD research is on the spatial variation of several air pollutants across Europe and modelling of concentrations of those pollutants with multi linear regression method in combination with land use information. The results of her PhD study are described in this thesis.

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I would like to thank Ingeborg, my co-promotor, who helped to initiate the whole process of my PhD study. Thank you for your support and sharing your experience during the past few years and helping me in combining regular work at TNO and completing my PhD.

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The ESCAPE and TRANSPHORM projects were the joint effort of many scientists across Europe, which is reflected in number of co-authors of the publications included in this book. I would like to thank all the partners involved in the work presented here for their help during the sampling campaign, data analysis and for their feedback on the publications.

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“Share the joy is twice as much fun, share your sorrow is half sorrow.” I am the one lucky person who has the amazing group of people around me with whom I share joy but also more difficult moments of my life, which makes my life so much nicer, easier and full of happiness.

I would like to thank my parents, family and friends in Poland. Thank you for your unconditional love and support I have experienced all my life.

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Acknowledgments

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