Modeling personal exposure to traffic related air pollutants

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Modeling personal exposure to traffic related air pollutants

Het modelleren van de persoonlijke blootstelling aan verkeers-gerelateerde luchtvervuiling (met een samenvatting in het Nederlands)

Proefschrift

ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus, prof. dr. G.J. van der Zwaan, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op donderdag 23 april 2015 des middags te 4.15 uur

door

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geboren op 23 februari 1985 te Leiden

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List of Abbreviations

BC	Black Carbon (soot)
COPD	Chronic Obstructive Pulmonary Disease
EC	Elemental Carbon
ETS	Environmental Tobacco Smoke
ESCAPE	European Study of Cohorts for Air Pollution Effects
GIS	Geographic Information System
HV	Hold-out Validation
HR	Hazard Ratio
PM	Particulate Matter
LOOCV	Leave One Out Cross Validation
LUR	Land Use Regression
MUSiC	Measurements of Ultrafine Particles and Soot in two Cities project
SD	Standard Deviation
SI	Supporting Information
RUPIOH	Study of the Relationship between Ultrafine and fine Particulate matter in Indoor and Outdoor air and respiratory Health
TAP	Time Activity Pattern
UFP	Ultrafine Particles
VE^{3}SPA	Validation of ESCAPE Exposure EstimateS using Personal exposure Assessment project

Chapter 1

General Introduction

Background

Numerous epidemiological studies have shown an association of long term exposure to air pollution and cardiovascular and respiratory health effects.[1,2] Presently, the link between air pollution exposure and adverse health effects is commonly accepted. Numerous studies suggest that elderly people are more vulnerable to the effects of air pollution. On the other hand, children are also thought to be more susceptible to the effects of air pollution than the general population, for example for respiratory diseases like asthma.[3]

Particulate air pollution contains emissions from both natural and man-made sources and can be classified by mass characteristics. Particulate matter with particulates smaller than 10 μm in diameter is known as PM_{10} and $PM_{2.5}$ has particulates smaller than 2.5 μm. Ultrafine particulate matter (UFP or $PM_{0.1}$) are particles of less than 100 nm in diameter. Variations in $PM_{2.5}$ constituents affect the toxicity and thus might have different health effects. Therefore determining the elemental composition of $PM_{2.5}$ is important.[4-7] In this thesis, we focus on the elements Cu, Zn, Fe, K, Ni, V, Si and S, which represent major sources of $PM_{2.5}$. NO_2 is a gaseous component that can be directly emitted from the engine (primary NO_2) or formed in the atmosphere from nitrogen oxide (NO) and ozone (O_3) (secondary NO_2).

To ascertain the true risk associated with exposure to air pollutants, accurate exposure assessment of the population is important. Traditionally, the exposure assessment in epidemiological studies relied on fixed monitoring network sites. However, this approach lacks particularly spatial resolution, which may mask exposure variability in the study population.[8] In an effort to gain more insight into spatial resolution, land use regression (LUR) models are used to predict ambient concentrations at residential level.

Recently, in the **E**uropean **S**tudy of **C**ohorts for **A**ir **P**ollution **E**ffects (ESCAPE) project, LUR models were developed to predict the ambient concentrations of PM_{10}, $PM_{2.5}$, NO_x and NO_2.[9] A total of 36 study areas, spread over Europe, were included in the project.[10] The land use regression models were developed by selecting 20 or 40 $PM_{2.5}$/PM_{10} and 40 or 80 NO_x/NO_2 sites with a large concentration contrast between sites. Geographic Information System (GIS) variables were entered into linear regression models to predict the mean concentrations measured at these sites. The developed LUR models were used to predict annual average outdoor air concentrations at residential addresses of cohort participants in epidemiological studies. For example, one of the ESCAPE studies assessed the effect of air pollution on natural-cause mortality.[11] In this study, a significant hazard ratio (HR) of 1.07 per 5 μg/m^3 was detected for $PM_{2.5}$.

For health risk assessment the personal exposure to air pollution is more relevant than outdoor air concentrations. People typically spend around 70-80% of their time indoors at home and spend long hours at work, at school or at other microenvironments.[12-14] Using solely outdoor predictions for the exposure assessment of study participants might lead to exposure misclassification, which reduces the ability of epidemiological studies to detect significant effects. However, personal monitoring of air pollution is time consuming and expensive. For large cohort studies, it is therefore more feasible to model the exposure. LUR models have the advantage of relatively simple input, relatively short computation time and fine spatial resolution of predictions. The agreement of predicted concentrations with actual personal exposure can be assessed by monitoring the personal exposure in a small study population. In addition, time activity patterns (TAP) need to be recorded to be able to include time spent at different microenvironments as a predictor. When people spent more time at home, we expect the home outdoor concentrations to be better correlated with personal measurements than when people spent more time at other locations. In this thesis the validity of using LUR models as a proxy for personal exposure is assessed.

Personal monitoring

Using ambient concentrations as a proxy for personal exposure is prone to measurement error.[15] Adjusting for this measurement error, using personal exposure samples from a validation study, can produce health effect estimates that are up to 2-3 times higher than when unadjusted outdoor concentrations are used.[16] The golden standard for personal exposure is measuring air pollution in the breathing zone of study participants. Most personal monitoring studies take a number of short term samples (24-48 h) for the exposure assessment for participants from groups sensitive to the effects of air pollution on health. For example, in a study in Vancouver 16 COPD patients were monitored for 7 times 24 hours.[17] A relatively low correlation of 0.48 (Pearson's R) was found for personal exposure and ambient $PM_{2.5}$ concentrations. In another study in Amsterdam and Helsinki, the indoor and personal exposure of elderly subjects, in total 37 and 48 respectively, was monitored for 24 hours every two weeks during 6 months.[18] The median Pearson's R between personal and outdoor $PM_{2.5}$ was 0.79 in Amsterdam and 0.76 in Helsinki. In a third study in Southern California, a panel of 24 school children with asthma were monitored for 10 days.[19] The Spearman correlation of $PM_{2.5}$ central site with personal measurements was 0.64. In a study by Liu et al., the personal exposure of 28 elderly people was measured for 5-16 times 24 hours, repeated measurements were spaced at least 24 hours apart. The observed Spearman correlation coefficient between personal and outdoor $PM_{2.5}$ concentrations was 0.33.[20] In New York, 40 children with asthma carried air pollution monitoring equipment for 1 month, 24 h per day. In this

study personal $PM_{2.5}$ was moderately correlated to outdoor concentrations (median Pearson's R=0.33).[21] One study compared modeled outdoor concentrations with personal exposures.[22] In this study, 63 children were monitored for 10-days (4 children concurrently). Separate models were developed for the 24-h average concentrations. The modeled outdoor $PM_{2.5}$ concentrations were associated with personal exposure, with an R^2 of 0.65-0.70. However, elemental carbon (EC) predictions were not associated with personal exposure.

The abovementioned studies are within-person studies, measuring temporal associations between ambient and personal concentrations. This approach is useful to study short-term effects of air pollution or for time-series studies. In contrast, land use regression models predict annual average concentrations, which can be used in studies of long-term health effects. Little is known about misclassification for these long-term exposure predictions. Therefore, it is necessary to validate LUR models with personal exposure monitoring.[23] Previously, only two studies have investigated the association of LUR models with personal exposure. In a study in Vancouver, LUR models predicted the personal exposure of pregnant women to NO and NO_2 but not $PM_{2.5}$ and soot.[24] In another Canadian study in Hamilton, no correlation was found between NO_2 LUR models and short-term indoor and personal exposure measurements.[25] In these studies, relatively short term personal exposure measurements were done and compared to LUR models. These short term personal exposure measurements might not be representative for annual average concentration, since temporal variations are more influential on short term measurements. This could explain the weak associations that were found between the models and personal measurements in these studies.

In a recent study, outdoor, indoor and personal $PM_{2.5}$ samples were collected for 2 consecutive days for 54 pregnant women in Barcelona.[26] Personal $PM_{2.5}$ concentrations were higher than the outdoor concentrations, and showed no between-person correlations with outdoor concentrations. However, outdoor Vanadium concentrations were correlated to the personal V concentrations with a Pearson's R^2 of 0.83. Outdoor-personal Black Smoke (BS), determined by the reflectance of the $PM_{2.5}$ filters, was moderately correlated with an R^2 of 0.31.

Mobile monitoring campaigns

Recent studies suggest that ultrafine particles (UFP) can be absorbed into systemic circulation and may be biologically more reactive than larger particles.[27] Furthermore, for UFP a routine monitoring network does not exist in the Netherlands. This emphasizes the need to develop methods for UFP exposure assessment in epidemiological studies. UFP number counts have large spatial variations and are not well correlated to mass data and are difficult to monitor with robust, affordable equipment. Building LUR

models for UFP is therefore much more challenging than for fine PM.

LUR models aimed at characterizing local air pollution levels in complex urban settings should be based on a large number of measurement sites.[28] When LUR models are built with a small amount of sites, overfitting of the model might be a problem.[29] A recent study suggests that when leave one out cross validation (LOOCV) is used to asses model fit, the predictive ability of the models is overestimated.[30] A better technique to test model fitting is hold-out validation (HV). To be able to perform HV, measuring at more sites is preferable. However, this reduces the available sampling time per site and/or increases cost. To measure in a time-effective way, it is feasible to have a mobile measurement platform. Several studies have relied on mobile monitoring to measure air pollution components.
For example, Larson et al. developed LUR models for soot. At 39 sites in Seattle a moving vehicle made a cloverleaf pattern through a central intersection for 5-13 minutes, passing the intersection four times. The developed model had an R^2 of 0.51.[31] In a German study, mobile measurements for $PM_{2.5}$ and PM_{10} were done for the total number of 59 monitoring sites. The regression model shows R^2 values of 0.77 (PM_{10}) and 0.61 ($PM_{2.5}$).[32]
Recently, some studies have developed LUR models for UFP.[33,34] These studies relied on data retrieved from mobile measurement campaigns, with relatively short sampling times. In Girona (Spain) UFP was measured for 15 minutes on the sidewalk of 644 participant's homes.[34] The core LUR model explained 36%. In Vancouver (Canada) at 80 sites UFP was monitored for 1 hour.[33] The resulting model had an R^2 of 0.48.

Aim of the thesis

For this thesis, I set up and conducted two projects; VE^{3}SPA and MUSiC. The objective of VE^{3}SPA was to quantify the agreement between LUR modeled concentrations and measured personal exposures for $PM_{2.5}$, soot, NO_2, Cu, Zn, Fe, K, Ni, V, Si and S. Furthermore, we determined the association of the temporal variation of the elemental composition of $PM_{2.5}$at a central monitoring site and personal exposure.
The aim of the MUSiC project was to build LUR models for BC and UFP using a mobile monitoring campaign. In addition, we evaluated the methodology of building LUR models using short term samples derived from mobile measurement campaigns. The validity of choosing short term samples at more sites over long term samples at fewer sites was investigated.

VE^{3}SPA study design

In the **V**alidation of **E**SCAPE **E**xposure **E**stimate**S** using **P**ersonal **A**ssessment (VE^{3}SPA) project LUR models, developed by the ESCAPE project, were

validated with personal exposure measurements. In Helsinki (Finland), Utrecht (the Netherlands) and Barcelona (Spain) 15 participants were selected from rural/semi-urban background, urban background and busy street sites. The measurements were carried out for six times 96 hours per participant, during three seasons (winter, summer and autumn/spring). During the measurements, participants followed prescribed time activity patterns, a child and elderly pattern. The study period ran from 01-03-2010 to 28-03-2011. The $PM_{2.5}$ samples were analyzed to determine the elemental composition. For this study the elements of interest were Cu, Zn, Fe, Ni, V, K, S and Si. All concentrations were adjusted for temporal variation using measurements from a reference site. Consecutively, the mean measured outdoor/indoor/personal concentrations per participant were calculated and the associations with the modeled concentrations were assessed.

MUSiC study design

The **M**easurements of **U**ltrafine particles and **S**oot **i**n two **C**ities project was a mobile measurement campaign. BC and UFP were measured real-time at 81 sites in Amsterdam and 80 sites in Rotterdam. The equipment was placed in an electrical car for transport. Continuous measurements were done for 30 minutes per site and repeated in three different seasons. Simultaneously, measurements at a reference site in Utrecht were collected. The study period was from January to July 2012. LUR models for BC and UFP were developed by adding GIS variables to the model with the ESCAPE selection method. Both spatial and temporal-spatial models were developed.

Outline of the thesis

In chapter 2, the associations of Land Use Regression models for $PM_{2.5}$, NO_2 and soot with personal measurements are discussed. The associations of the $PM_{2.5}$ elemental components with LUR models for these elements are discussed in chapter 3. In chapter 4, temporal associations of the measured elemental composition of $PM_{2.5}$ at a central site and personal exposure are assessed. Chapter 5 and 6 describe the results for the MUSiC project. In Chapter 5, methodological aspects of mobile measurement campaigns are assessed. In chapter 6 , LUR models for UFP and BC are developed.

References

1. Pope III, C.A. and Dockery, D.W. Health effects of fine particulate air pollution: Lines that connect. *EM: Air and Waste Management Association's Magazine for Environmental Managers* **2006,** *54,* 709-742.

2. Brunekreef, B. and Holgate, S.T. Air pollution and health. *Lancet* **2002,** *360,* 1233-1242.

3. Sacks, J.D.; Stanek, L.W.; Luben, T.J., et al Particulate matter-induced health effects: who is susceptible? *Environ. Health Perspect.* **2011,** *119,* 446-454.

4. Jalava, P.I.; Salonen, R.O.; Pennanen, A.S., et al Heterogeneities in inflammatory and cytotoxic responses of RAW 264.7 macrophage cell line to urban air coarse, fine, and ultrafine particles from six European sampling campaigns. *Inhal. Toxicol.* **2007,** *19,* 213-225.

5. Dominici, F.; Peng, R.D.; Bell, M.L., et al Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *J. Am. Med. Assoc.* **2006,** *295,* 1127-1134.

6. Peng, R.D.; Dominici, F.; Pastor-Barriuso, R.; Zeger, S.L.; Samet, J.M. Seasonal analyses of air pollution and mortality in 100 US cities. *Am. J. Epidemiol.* **2005,** *161,* 585-594.

7. Kelly, F.J. Oxidative stress: Its role in air pollution and adverse health effects. *Occup. Environ. Med.* **2003,** *60,* 612-616.

8. Ozkaynak, H.; Baxter, L.K.; Dionisio, K.L.; Burke, J. Air pollution exposure prediction approaches used in air pollution epidemiology studies. *J. Expo. Sci. Environ. Epidemiol.* **2013,** *23,* 566-572.

9. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. *Environ. Sci. Technol.* **2012,** *46,* 11195-11205.

10. Cyrys, J.; Eeftens, M.; Heinrich, J., et al Variation of NO2 and NOx concentrations between and within 36 European study areas: Results from the ESCAPE study. *Atmos. Environ.* **2012,** *62,* 374-390.

11. Beelen, R.; Raaschou-Nielsen, O.; Stafoggia, M., et al Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project. *The Lancet* **2014,** *383,* 785-795.

12. Brasche, S. and Bischof, W. Daily time spent indoors in German homes - Baseline data for the assessment of indoor exposure of German occupants. *Int. J. Hyg. Environ. Health* **2005,** *208,* 247-253.

13. Triadó, C.; Villar, F.; Solé, C.; Celdrán, M.; Osuna, M.J. Daily activity and life satisfaction in older people living in rural contexts. *Spanish Journal of Psychology* **2009,** *12,* 236-245.

14. Brunekreef, B.; Janssen, N.A.; de Hartog, J.J., et al Personal, indoor, and outdoor exposures to PM2.5 and its components for groups of cardiovascular patients in Amsterdam and Helsinki. *Res. Rep. Health Eff. Inst.* **2005,** 1-70; discussion 71-79.

15. Avery, C.L.; Mills, K.T.; Williams, R., et al Estimating error in using ambient PM2.5 concentrations as proxies for personal exposures: A review. *Epidemiology* **2010,** *21,* 215-223.

16. Van Roosbroeck, S.; Li, R.; Hoek, G.; Lebret, E.; Brunekreef, B.; Spiegelman, D. Traffic-related outdoor air pollution and respiratory symptoms in children: The impact of adjustment for exposure measurement error. *Epidemiology* **2008,** *19,* 409-416.

17. Ebelt, S.T.; Petkau, A.J.; Vedal, S.; Fisher, T.V.; Brauer, M. Exposure of chronic obstructive pulmonary disease patients to particulate matter: Relationships between personal and ambient air concentrations. *J. Air Waste Manage. Assoc.* **2000,** *50,* 1081-1094.

18. Janssen, N.A.H.; De Hartog, J.J.; Hoek, G., et al Personal exposure to fine particulate matter in elderly subjects: Relation between personal, indoor, and outdoor concentrations. *Journal of the Air and Waste Management Association* **2000,** *50,* 1133-1143.

19. Delfino, R.J.; Staimer, N.; Gillen, D., et al Personal and ambient air pollution is associated with increased exhaled nitric oxide in children with asthma. *Environ. Health Perspect.* **2006,** *114,* 1736-1743.

20. Liu, L.; Ruddy, T.; Dalipaj, M., et al Effects of indoor, outdoor, and personal exposure to particulate air pollution on cardiovascular physiology and systemic mediators in seniors. *Journal of Occupational and Environmental Medicine* **2009,** *51,* 1088-1098.

21. Spira-Cohen, A.; Chen, L.C.; Kendall, M.; Lall, R.; Thurston, G.D. Personal exposures to traffic-related air pollution and acute respiratory health among bronx schoolchildren with asthma. *Environ. Health Perspect.* **2011,** *119,* 559-565.

22. Ducret-Stich, R.; Delfino, J.; Tjoa, T., et al Home outdoor models for traffic-related air pollutants do not represent personal exposure measurements in Southern California. *J. Phys. Conf. Ser.* **2009,** *151,*

23. Hoek, G.; Beelen, R.; de Hoogh, K., et al A review of land-use regression models to assess spatial variation of outdoor air pollution. *Atmos. Environ.* **2008,** *42,* 7561-7578.

24. Nethery, E.; Teschke, K.; Brauer, M. Predicting personal exposure of pregnant women to traffic-related air pollutants. *Sci. Total Environ.* **2008,** *395,* 11-22.

25. Sahsuvaroglu, T.; Su, J.G.; Brook, J.; Burnett, R.; Loeb, M.; Jerrett, M. Predicting personal nitrogen dioxide exposure in an elderly population: Integrating residential indoor and outdoor measurements, fixed-site ambient pollution concentrations, modeled pollutant levels, and time-activity patterns. *J. Toxicol. Environ. Health Part A Curr. Iss.* **2009,** *72,* 1520-1533.

26. Minguillón, M.C.; Schembari, A.; Triguero-Mas, M., et al Source apportionment of indoor, outdoor and personal PM 2.5 exposure of pregnant women in Barcelona, Spain. *Atmos. Environ.* **2012,** *59,* 426-436.

27. HEI Review Panel Understanding the Health Effects of Ambient Ultrafine Particles Report. *Health Effects Institute* **2013,** *January,* HEI Perspectives 3.

28. Basagaña, X.; Rivera, M.; Aguilera, I., et al Effect of the number of measurement sites on land use regression models in estimating local air pollution. *Atmos. Environ.* **2012,** *54,* 634-642.

29. Babyak, M.A. What you see may not be what you get: A brief, nontechnical introduction to overfitting in regression-type models. *Psychosom. Med.* **2004,** *66,* 411-421.

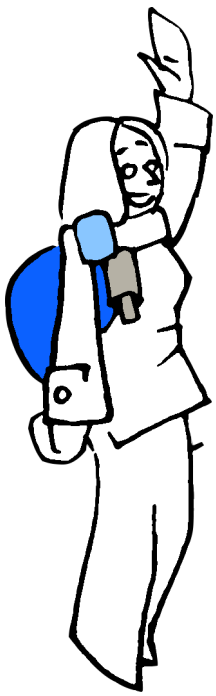
30. Wang, M.; Beelen, R.; Basagana, X., et al Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project. *Environ. Sci. Technol.* **2013,** *47,* 4357-4364.

31. Larson, T.; Hernderson, S.; Brauer, M. Mobile monitoring of particle light absorption coefficient in an urban area as a basis for land use regression. - *Environ Sci Technol* **2009,** 4672-4678.

32. Merbitz, H.; Fritz, S.; Schneider, C. Mobile measurements and regression modeling of the spatial particulate matter variability in an urban area. *Sci. Total Environ.* **2012,** *438,* 389-403.

33. Abernethy, R.C.; Allen, R.W.; McKendry, I.G.; Brauer, M. A Land Use Regression Model for Ultrafine Particles in Vancouver, Canada. *Environ. Sci. Technol.* **2013,** *47,* 5217–5225.

34. Rivera, M.; Basagaña, X.; Aguilera, I., et al Spatial distribution of ultrafine particles in urban settings: A land use regression model. *Atmos. Environ.* **2012,** *54,* 657-666.



Chapter 2

Agreement of Land Use Regression Models with Personal Exposure Measurements of Particulate Matter and Nitrogen Oxides Air Pollution

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Abstract

Land use regression (LUR) models are often used to predict long-term average concentrations of air pollutants. Little is known how well LUR models predict personal exposure. In this study the agreement of LUR models with measured personal exposure was assessed. The measured components were particulate matter with a diameter smaller than 2.5 μm ($PM_{2.5}$), soot (reflectance of $PM_{2.5}$), nitrogen oxides (NO_x) and nitrogen dioxide (NO_2). In Helsinki, Utrecht and Barcelona, 15 volunteers (from semiurban, urban background and traffic sites) followed prescribed time activity patterns. Per participant, six 96 h outdoor, indoor and personal measurements spread over three seasons were conducted. Soot LUR models were significantly correlated with measured average outdoor and personal soot concentrations. Soot LUR models explained 39%, 44% and 20% of personal exposure variability (R^2) in Helsinki, Utrecht and Barcelona. NO_2 LUR models significantly predicted outdoor concentrations and personal exposure in Utrecht and Helsinki, whereas NO_x and $PM_{2.5}$ LUR models did not predict personal exposure. $PM_{2.5}$, NO_2 and NO_x models were correlated with personal soot, the component least affected by indoor sources. LUR modeled and measured outdoor, indoor and personal concentrations were highly correlated for all pollutants when data from the three cities were combined. This study supports the use of intra-urban LUR models for especially soot in air pollution epidemiology

Introduction

Land use regression (LUR) models are frequently used for exposure assessment in epidemiological studies of long-term air pollution exposure.[1] Such models predict fine scale spatial variation of ambient concentrations, often at the residential address. However, this is not the same as personal exposures. Little is known how well LUR models predict average personal exposure.[1] Sahsuvaroglu et al. found no correlation between NO_2 LUR models and short-term indoor and personal exposure measurements.[2] Nethery et al. found that LUR models predicted personal exposure of pregnant women to NO and NO_2 but not $PM_{2.5}$ and soot.[3] A challenge identified in these studies was to obtain sufficient measurements to assess long-term average personal exposure.

In the VE^{3}SPA project **(V**alidation of **E**SCAPE **E**xposure **E**stimate**S** using **P**ersonal exposure **A**ssessment), outdoor, indoor and personal concentrations of soot, nitrogen dioxide (NO_2), nitrogen oxides (NO_x) and particulate matter less than 2.5 µm in diameter ($PM_{2.5}$) were measured by volunteers from three selected areas in Europe. The objective of VE^{3}SPA was to quantify the agreement between LUR modeled annual outdoor concentrations at the home (school address) and annual personal exposures based on the soot, NO_2, NO_x and $PM_{2.5}$ measurements. LUR models were developed in the framework of the European Study of Cohorts for Air Pollution Effects (ESCAPE), an EU funded project that studies the effect of long-term air pollution exposure on health effects in 20 European study areas.[4-6]

Materials and Methods

Study Design

The study was conducted in and near three ESCAPE cities: in Utrecht, the Netherlands (NL), Barcelona, Spain (ES) and Helsinki, Finland (FI) to represent Western, Southern and Northern European settings. In each city 15 volunteers participated: five living at a traffic site, five at an urban background location and five living at a semiurban/regional background location. The personal exposure to soot, $PM_{2.5}$, NO_2, NO_x and the elemental composition of $PM_{2.5}$ were measured concurrent with indoor and outdoor measurements. The results for the elemental composition of $PM_{2.5}$ will be reported elsewhere.

For each participant, six 96-hour samples were collected spread over three seasons (summer, winter and intermediate) from Monday to Friday. In each season, two prescribed time activity patterns (TAP) were followed, representative for a school child and an elderly person. Because of logistics, three persons were measured simultaneously. During every measuring period samples were simultaneously collected at a reference site to

correct for temporal variation related to weather conditions.

Methods were standardized for the three cities. A standard operating manual was developed and a workshop was organized for the field technicians (http://www.escapeproject.eu/vespa/manual.php). All lab and data analyses were centrally performed in Utrecht, the same equipment was used and site visits to Helsinki and Barcelona were organized to check that field procedures were followed according to the manual.

We analyzed the correlation between LUR model predictions at the home (and school) address and the average measured outdoor, indoor and personal concentrations. Our main analysis is on within-city correlations, but we also evaluated the correlation combining the data from the three cities.

Volunteer and Site Selection

Fifteen non-smoking volunteers were selected by their home address to represent the variability in outdoor concentrations in the ESCAPE study. The aim was to have enough variability in outdoor concentration at the addresses to be able to investigate the correlation between the ESCAPE modeled outdoor concentrations and personal exposure. Therefore five traffic, five urban background and five semiurban background sites were selected. Background sites were defined as carrying less than 3000 vehicles per day in a 50 m circle with no other local sources. Traffic sites were defined as in ESCAPE as streets carrying more than 10 000 vehicles per day.

Time Activity Pattern

Past work has shown that it is very time consuming to recruit, instruct and maintain a pool of volunteers from the general population, and that the information obtained is sometimes not optimal in terms of distribution of relevant time activity patterns, microenvironments, indoor sources and so forth.[7] For this reason we selected volunteers willing to conduct the measurements according to predefined time activity patterns. Since children and elderly adults are considered to be subgroups sensitive to the health effects of air pollution, two time activity patterns were developed. Between the three cities there were some minor differences between the time activity patterns to represent the differences in lifestyle between these cities. More detail can be found in the VE^{3}SPA study manual (http://www.escapeproject.eu/vespa).

During both time activity patterns, the volunteers spend the majority of their time at home. Every volunteer had a "fixed indoor" (or "school") location during the children's pattern. For this location the outdoor

concentration could also be modeled and thus we could evaluate whether we can improve upon the model with the home address only by adding the predicted concentrations at the school. For the elderly pattern, the volunteers were instructed to go to different types of locations such as the house of a friend. During both time activity patterns, volunteers were instructed to spend two hours outdoors, including time spent commuting by car, bus or bicycle. Time activity diaries were entered by the volunteers in a special designed Excel file with an hourly resolution during each 96 h sampling period.

Sampling and Analyses

BGI 400s personal sampling pump units (BGI Inc., Waltham, MA) were used for $PM_{2.5}$ sampling on Teflon filters (Zefon international, Ocala FL). Ogawa diffusion badges (Ogawa & Company USA Inc., Pompano Beach FL) were used for NO_x and NO_2 sampling. For every participant indoor, outdoor and personal samples were taken. Sampling site criteria were based upon RUPIOH[8] and are listed in detail in the study manual (www.escapeproject.eu/vespa). Criteria for the outdoor site included that the monitoring site had to be on the street side for traffic locations, on the same height as the living-room and not placed near exhaust flues or vents. Criteria for the indoor site included sampling height between 1 and 2 meters, two meters away from doors, windows or other ventilation inlets and more than 2 m away from sources (gas range). Personal pump units were carried by participants in backpacks, with the sampling cyclones (GK 2.05 KTL, BGI Inc., Waltham, MA) at shoulder height.

The flow of the pump units was measured before and after sampling with calibrated rotameters (Brooks Instruments, Hatfield, PA). Elapsed time counters (ETC) of the units were used to record the total sampling time. The study period ran from 01-03-2010 to 28-03-2011. In Utrecht and Barcelona these periods were mainly after the ESCAPE study period; in Helsinki study periods in VE[3]SPA and ESCAPE overlapped substantially. Three subjects were measured simultaneously, the goal was to have the three residential types (S, UB, RB) represented in each sampling period. All samples were prepared and analyzed centrally in Utrecht (IRAS, Utrecht) and cooled during transport.

$PM_{2.5}$ concentrations were determined by pre- and postweighing of the Teflon filters, following ESCAPE procedures.[4] The reflectance of these Teflon filters was measured with the Smoke Stain Reflectometer model M43D (Diffusion systems, London UK). The reflectance was transformed into absorbance (a) according to ISO 9835

$a = (A/2V) \times \ln (R_0/Rs)$ [9]

where A is the loaded filter area (m^2), V is the sampled volume (m^3), R_0 is the average reflectance of field blank filters, and Rs is the reflectance

of the sampled filter. Absorbance was expressed in 10^{-5} m^{-1}. Absorbance correlates well with actual measurements of elemental carbon (soot).[10-12] We will use the term soot hereafter.

$PM_{2.5}$ measurements were discarded if the elapsed time counter (ETC) showed that the unit had run less than 60% of the target of 5760 minutes and/or if the end flow of the pump unit was not within 35% of 3.5 l/m. NO_2 and NO_x badges were analyzed using a spectrophotometer based upon the Saltzman method,[13] following ESCAPE procedures. From each batch of 40 badges, four were kept at the IRAS laboratory as lab blanks. These lab blanks were analyzed on the same day as the sampled badges from that batch and their average concentrations were subtracted from the sampled concentrations. For quality assurance and control the aim was to have 15 duplicates and field blanks for each city, 7 taken indoors and 8 at the reference site/outdoors. In addition, five personal exposure duplicates were carried out by volunteers outside the main study period.

To be able to correct for differences in temporal variation related to weather conditions during sampling periods, a reference site was chosen for each study area. Measurements were conducted at the reference sites during every 96 hour measuring period. The reference sites were placed at background sites. In Helsinki and Utrecht, the reference site was at the same location as the reference site for ESCAPE.[14] In Barcelona, the reference site was on a different location than the ESCAPE reference site, at around 300 meters away from the sea.

Land Use Regression Models

We used the Land Use Regression models developed in ESCAPE.[5,15] The models are summarized in the supporting information (supporting information 1, SI1). The models were developed for the entire Netherlands, Helsinki + Turku and Barcelona. The models were applied to the home and school addresses of all participants to predict annual averages of $PM_{2.5}$, soot, NO_x and NO_2 concentrations. GIS predictors were truncated to the range at the measurement sites.[16] The outdoor concentrations were calculated for the exact home location (within a few meters) of each VE^{3}SPA participant.

Data Analysis

Linear regression analyses were performed to assess within city associations between the LUR *modeled* outdoor concentration and the *measured* average outdoor, indoor and personal concentrations. We evaluated the explained variance (R^2) and the regression slope. We also assessed the association between modeled and measured exposures in a pooled dataset combining the three cities, relevant for studies assessing both within and between city associations of air pollution and health.

For every participant the average of the six measurements was calculated with adjustment for temporal variation using data from the reference site. For the outdoor measurements, the difference at the reference site from the annual mean at the reference site was subtracted from the measurement, as in ESCAPE.[4] Personal and indoor measurements were probably less influenced by temporal differences than outdoor concentrations. The adjustment therefore involved the outdoor difference multiplied by the regression slopes of the linear relationship of the outdoor measurements with the indoor and personal measurements determined in each city. As slopes were below 1, the adjustment for the indoor and personal measurements was smaller than for the outdoor measurements. SI2 (Supporting Information) provides a more detailed explanation, including the slopes used for adjustment in each city. In The Netherlands and Spain, occasionally missing reference site data were imputed using a regression model between the reference site data and data from continuous routine monitoring sites (SI2).

In an additional analysis we included the average reference site concentration during the six sampling sessions as a predictor variable in a regression model with the unadjusted average as the dependent variable and the modeled concentration as the independent variable. We also adjusted for indoor sources during the sampling period; environmental tobacco smoke (ETS), gas cooking, floor cover, air conditioning, heating and owning a pet. ETS exposure occurred in the other indoor environments or at home when visitors smoked. These factors were added to the general linear model as binary variables. Regression analyses were also performed separately for the child and elderly TAP. We investigated whether adding the modeled concentration at the school location improved the prediction of personal exposure by specifying a time-weighted model. The amount of time spent at home was multiplied with the modeled home outdoor concentrations and added to the time weighted modeled school outdoor concentrations. This was divided by the sum of time spent at home and at school.
Linear regression analyses were also performed to assess the relationship between the average *measured* outdoor, indoor and personal concentrations.

Finally, we investigated the association between the modeled $PM_{2.5}$, NO_2 and NO_x outdoor concentrations and the measured soot personal exposure (Supporting Information, SI3). We performed this analysis because soot is less affected by indoor sources than the other pollutants. This analysis was motivated by work of Sarnat and co-workers who showed that the temporal correlation of ambient gases with personal $PM_{2.5}$ was higher than with personal exposure of the same gas (O_3, NO_2).[17] For all statistical analysis the Statistical Analysis System (SAS) software, version 9.2 was used.

Results

Study Population

Figure S1 in SI4 (supporting information) shows the location of the volunteer home addresses in the three study areas. In Utrecht and Helsinki, there are large differences between the site types in traffic intensities at the nearest road, with very low counts at urban background locations and even lower at semi urban background locations (SI4). In Barcelona there is also a clear contrast between site types; the traffic intensity is very high at the street sites and very low at the semiurban background sites. However, at the urban background locations in Barcelona traffic intensity is relatively high. In Helsinki, sampling heights were highest at the street sites and next urban background sites. This may have reduced the contrast in air pollution related to differences in traffic intensity. In Utrecht and Barcelona differences in sampling height were smaller.

There were differences in possible indoor sources between the three cities (SI4). In Barcelona more people had air conditioning and less had central heating compared to those in Helsinki and Utrecht. Furthermore, the majority was cooking on gas in Utrecht and Spain and no one had an open kitchen in Spain, whereas most people in Utrecht and Helsinki had.

Table 1 The total number of hours that were spent on average by the volunteers at three microenvironments (at home, outdoors and other indoor locations) per 96 hours.

Child Pattern	Home			Outdoors			Other indoor		
	Goal	Mean	SD	Goal	Mean	SD	Goal	Mean	SD
Utrecht	64	63.9	3.7	8.0	8.0	2.1	24.0	23.9	2.7
Barcelona	52	57.4	9.5	12.0	8.6	2.1	32.0	29.9	8.6
Helsinki	68	66.6	5.4	8.0	3.5	1.1	20.0	24.1	4.0
Elderly Pattern	**Home**			**Outdoors**			**Other indoor**		
	Goal	**Mean**	**SD**	**Goal**	**Mean**	**SD**	**Goal**	**Mean**	**SD**
Utrecht	72	70.9	3.6	8.0	8.4	2.1	12.0	15.9	3.5
Barcelona	68	62.6	8.6	8.0	8.0	3.8	20.0	23.7	8.9
Helsinki	80	78.0	6.7	4.0	2.2	0.7	12.0	13.6	4.0

Goal is the prescribed amount of time to be spent at the microenvironment per 96 h. Mean is the actual mean number of hours that were spent at the microenvironment by the participants. SD is the standard deviation of the number of hours spend by the participants.

Descriptive Results

Overall, the participants managed to follow the pattern very well during the measuring weeks (Table 1). There was a clear difference in the amount

of time spent at the other indoor locations between the two patterns in all three cities. In Barcelona, the contrast between the child and the elderly pattern was not as clear as was prescribed – the difference between the patterns on the time spent at home was, on average, only 6 hours instead of the 16 hours that were prescribed).

Overall, detection limits calculated from the field blanks were low (SI5). The soot measurements were all above the detection limit (DL), most $PM_{2.5}$ and NO_2 as well. The measurements that were below the detection limit were included in the analysis. Most coefficients of variation for the duplicate measurements are about 10% (Supporting Information, SI5).

The measured concentrations of all four components were highest in Barcelona and lowest in Helsinki at all three site types. The range in measured $PM_{2.5}$ concentrations was small, especially in Helsinki (Table 2).

Table 2 The mean (min-max) of the $PM_{2.5}$ (μg/m³), soot (10^{-5} m^{-1}), NO_2 (μg/m³) and NO_x (μg/m³) concentrations of the average concentrations per site, per city (N=15).

		Utrecht	Barcelona	Helsinki
$PM_{2.5}$	Modeled	17.1 (14.5-19.2)	18.1 (13.6-25.1)	8.5 (7.7-9.5)
	Outdoor	15.3 (11.5-19.7)	17.5 (12.6-23.1)	7.0 (5.4-8.9)
	Indoor	12.0 (7.2-20.5)	16.5 (11.4-28.0)	7.6 (3.2-22.5)
	Personal	11.2 (8.5-14.7)	21.7 (13.4-47.0)	6.4 (2.9-11.4)
Soot	Modeled	1.5 (1.1-2.1)	2.9 (1.7-4.0)	1.1 (1.0-1.4)
	Outdoor	1.3 (0.9-2.4)	2.6 (1.7-3.7)	0.9 (0.6-1.4)
	Indoor	1.1 (0.7-1.7)	2.1 (1.4-3.1)	0.8 (0.4-1.7)
	Personal	1.0 (0.7-1.3)	2.2 (1.6-2.8)	0.8 (0.4-1.5)
NOx	Modeled	43.3 (26.0-74.6)	102.1 (56.4-184.1)	32.1 (19.1-57.9)
	Outdoor	58.4 (31.4-108.5)	120.9 (77.9-232.9)	38.4 (25.7-60.3)
	Indoor	55.3 (23.8-98.4)	110.2 (70.4-175.4)	39.6 (18.7-152.8)
	Personal	50.5 (30.1-73.0)	111.0 (84.0-157.0)	40.9 (16.5-130.1)
NO_2	Modeled	27.4 (18.5-40.4)	59.1 (33.1-85.9)	19.7 (13.2-30.9)
	Outdoor	33.7 (20.4-50.9)	69.8 (49.0-103.1)	26.0 (17.0-40.0)
	Indoor	23.7 (14.3-35.9)	52.0 (30.4-66.9)	16.7 (8.1-40.1)
	Personal	23.8 (16.9-29.7)	51.4 (42.1-69.4)	17.4 (9.8-31.0)

The average concentration per site were calculated. Then the mean, minimum and maximum from these site averages was determined.

Association between Modeled and Measured Concentrations

The associations of the outdoor concentrations predicted by the ESCAPE LUR models with the mean adjusted measured outdoor, indoor and personal concentrations are shown in Table 3 and the scatterplots in Figure 1 and SI6. The LUR models predicted the *outdoor* soot, NO_2 and NO_x concentrations well, especially in Utrecht and Helsinki. For *outdoor* $PM_{2.5}$ the percentage explained variability (R^2) of the LUR models was lower and only significant in Utrecht and (borderline) in Helsinki.

For soot, the measured *indoor* and *personal* concentrations were associated with the modeled concentrations in Utrecht, Barcelona and Helsinki. However, correlations were lower than for the measured *outdoor* concentrations.

Table 3 The relationship between LUR modeled outdoor concentrations and measured average outdoor/indoor/personal concentrations (N=15).

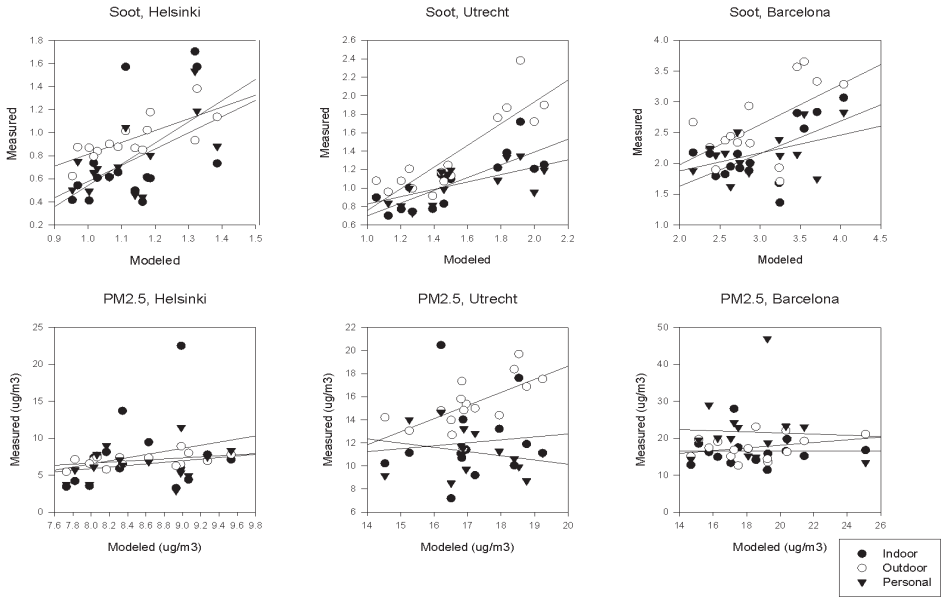
Measurements		Outdoor			Indoor			Personal		
Component	city	R^2	β	p	R^2	β	p	R^2	β	p
$PM_{2.5}$	Utrecht	0.43	1.09	0.01	0.01	0.26	0.72	0.06	-0.37	0.36
	Helsinki	0.21	0.72	0.08	0.06	2.10	0.38	0.08	1.08	0.32
	Barcelona	0.10	0.37	0.25	0.00	0.00	0.99	0.00	-0.15	0.86
Soot	Utrecht	0.75	1.18	0.00	0.64	0.69	0.00	0.44	0.40	0.01
	Helsinki	0.57	1.02	0.00	0.30	1.84	0.03	0.39	1.41	0.01
	Barcelona	0.33	0.65	0.02	0.36	0.53	0.02	0.20	0.29	0.09
NO_2	Utrecht	0.82	1.13	0.00	0.37	0.57	0.02	0.35	0.33	0.02
	Helsinki	0.55	0.87	0.00	0.05	0.36	0.41	0.20	0.50	0.09
	Barcelona	0.49	0.87	0.00	0.06	0.22	0.38	0.03	0.11	0.56
NO_x	Utrecht	0.74	1.41	0.00	0.21	0.71	0.09	0.13	0.37	0.19
	Helsinki	0.41	0.61	0.01	0.01	-0.35	0.70	0.01	-0.29	0.68
	Barcelona	0.50	0.94	0.00	0.23	0.43	0.07	0.06	0.18	0.36

Concentrations adjusted using the adjusted average method. The coefficient of determination (R^2), the regression coefficient (β), and the p value (p) of the β

The modeled outdoor NO_2 concentrations were associated with measured *personal* NO_2 concentrations in Utrecht and Helsinki (borderline) but not in Barcelona. For $PM_{2.5}$ and NO_x, no consistent associations were found between modeled outdoor concentrations and measured *indoor* and *personal* concentrations. Associations were similar for the alternative temporal adjustment method (SI7).

Highly significant associations between LUR modeled and measured outdoor, indoor and personal concentrations for all pollutants were found in the pooled dataset (Table 4). Consistent with the within-city analysis, the highest R^2 for the association between modeled and personal concentrations was found for soot (R^2 = 83%) and the lowest for $PM_{2.5}$ (R^2 = 35%). When indicator variables for city were added to the model, soot and NO_2 personal exposure remained significantly associated with the modeled concentrations. Associations for $PM_{2.5}$ and NO_x were not significant anymore.

Figure 1 Regression plots of the corrected measured average versus modeled concentration for $PM_{2.5}$ and Soot in Helsinki, Utrecht and Barcelona.



Inclusion of the indoor sources ETS, cooking on gas, owning a pet and the type of floor cover (smooth floor, carpet or a smooth floor with a rug larger than 1 m^3) to the model did not significantly influence the R squares and the slopes of the association between modeled and measured concentrations (data not shown). Restriction to observations without reported ETS also did not affect associations (SI8).

A time-weighted model including the school location did not improve the personal exposure model much. R^2 of the models ranged from 35 to 57% for soot (compared to 20-44% for the home, Table 3) and 4 to 16% for $PM_{2.5}$ (compared to 0 – 8% for the home). There was no consistent difference in correlation when stratifying for the child and elderly pattern. Interaction terms were not statistically significant (data not shown).

Table 4 The relationship between LUR modeled outdoor concentrations and measured adjusted average concentrations (data of the three cities combined).

	Outdoor						
	without city indicators				with city indicators		
	N	R^2	β	p	R^2	βmod	pmod
$PM_{2.5}$	45	0.81	0.97	0.00	0.84	0.50	0.01
Soot	45	0.85	0.88	0.00	0.85	0.80	0.00
NO_2	45	0.91	1.07	0.00	0.91	0.94	0.00
NO_x	45	0.81	1.09	0.00	0.82	0.98	0.00
	Indoor						
	without city indicators				with city indicators		
	N	R^2	β	p	R^2	βmod	pmod
$PM_{2.5}$	45	0.35	0.68	0.00	0.46	0.12	0.74
Soot	45	0.79	0.72	0.00	0.79	0.63	0.00
NO_2	45	0.74	0.76	0.00	0.79	0.33	0.04
NO_x	45	0.51	0.78	0.00	0.56	0.40	0.06
	Personal						
	without city indicators				with city indicators		
	N	R^2	β	p	R^2	βmod	pmod
$PM_{2.5}$	45	0.35	1.01	0.00	0.63	-0.15	0.74
Soot	45	0.83	0.70	0.00	0.86	0.37	0.00
NO_2	45	0.79	0.72	0.00	0.87	0.22	0.05
NO_x	45	0.54	0.73	0.00	0.67	0.17	0.30

The number of measurements (N), the coefficient of determination (R^2), the regression coefficient (β) and the p-value (p) of the β of the adjusted measured concentrations versus the modeled concentrations (outdoor, exact location). The second R^2 is of the analysis with an indicator for city included in the model. βmod and pmod are the β and the p-value of the modeled concentrations for this analysis.

Additional Analyses

Personal soot versus modeled outdoor $PM_{2.5}$, NO_2 and NO_x

Modeled outdoor $PM_{2.5}$, NO_2 and NO_x concentrations were statistically significantly correlated with measured personal soot in Utrecht and Helsinki (SI3). In Barcelona only the modeled NO_x concentration was (borderline) significantly associated with personal soot.

Measured indoor/personal versus measured outdoor

Overall, *measured* outdoor concentrations correlated only moderately better with measured personal and indoor concentrations than *modeled* concentrations (Table 5) For most components the indoor measurements were better correlated to the personal measurements than the outdoor measurements, especially for NO_2 and NO_x (Table 5).

Discussion

Overall, the ESCAPE LUR models predicted measured outdoor soot, NO_2 and NO_x concentrations well. The outdoor $PM_{2.5}$ concentrations were less well predicted, only in Utrecht this association was significant. The ESCAPE models for soot were associated with indoor and personal concentrations in all three cities. For NO_2, the personal and indoor concentrations were associated with modeled concentration in Utrecht and (borderline) in Helsinki. Personal exposure to $PM_{2.5}$ and NO_x were not associated with the modeled outdoor concentration in any of the three cities. LUR modeled and measured outdoor, indoor and personal concentrations were highly correlated for all pollutants when data from the three cities were combined.

Table 5 The relationship between measured average outdoor concentrations, measured indoor/personal concentrations and measured indoor with personal concentrations (N=15).

		Outdoor vs Indoor			Outdoor vs Personal			Indoor vs Personal		
		R^2	β	p	R^2	β	p	R^2	β	p
$PM_{2.5}$	Utrecht	0.01	0.08	0.67	0.09	-0.34	0.28	0.15	0.68	0.16
	Helsinki	0.29	0.10	0.04	0.32	0.23	0.03	0.61	1.73	0.00
	Barcelona	0.00	0.03	0.90	0.10	-0.12	0.25	0.02	-0.07	0.60
Soot	Utrecht	0.86	1.46	0.00	0.53	1.66	0.00	0.79	1.28	0.00
	Helsinki	0.27	0.21	0.05	0.29	0.32	0.04	0.85	1.37	0.00
	Barcelona	0.76	1.12	0.00	0.04	0.36	0.46	0.11	0.44	0.24
NO_2	Utrecht	0.26	0.69	0.05	0.30	1.20	0.04	0.38	1.02	0.01
	Helsinki	0.08	0.21	0.30	0.30	0.58	0.03	0.61	1.11	0.00
	Barcelona	0.05	0.30	0.43	0.08	0.53	0.30	0.32	0.77	0.03
NO_x	Utrecht	0.39	0.66	0.01	0.27	0.83	0.05	0.71	1.27	0.00
	Helsinki	0.00	0.02	0.82	0.01	0.03	0.78	0.95	1.29	0.00
	Barcelona	0.68	1.23	0.00	0.45	1.24	0.01	0.60	0.96	0.00

The coefficient of determination (R^2), the regression coefficient (β) and the p value (p) of the regression analysis

LUR Modeled and Measured Outdoor Concentrations

For all pollutants the R^2 of the regression models of modeled versus measured outdoor concentration was lower than the model and cross-validation R^2 of the LUR models.[5] This is consistent with recent studies on NO_2, showing that the model R^2 overestimates the predictive ability of the model in independent datasets.[16,18] The LUR models nevertheless predicted a substantial amount of ambient variation, particularly if we take into account that the study area for model development was larger than the study area for personal monitoring: entire Netherlands versus Utrecht and surroundings; Helsinki and Turku area versus Helsinki. For Barcelona the study area was the same size. There was a relatively small variation of the measured outdoor $PM_{2.5}$ concentration compared to the ESCAPE project, particularly in Helsinki.[4] This has probably contributed to the limited agreement with the LUR model. Although the overall pattern of associations were reasonably consistent across the cities e.g. with fairly clear associations for soot and lower correlations for $PM_{2.5}$, correlations were generally highest in Utrecht and lowest in Barcelona. We do not have a clear explanation for the different performance of the models between the three cities. One explanation is simply: chance. As we have shown in two recent papers on validation of LUR models, having small numbers of sites available for 'training' and then 'testing (validating)' the models produces a fair amount of random variation the validation R^2s.[16,18] We tend to not put too much weight on the differences in performance between the three cities in this exercise. Another explanation for the outdoor concentrations could be that the Dutch models were based on 40 $PM_{2.5}$ sites and 80 NO_x/NO_2 sites, whereas the Spanish and Finnish models were based on 20 $PM_{2.5}$ and 40 NO_x/NO_2 sites. Recent methodological studies have documented that LUR models based on larger datasets have slightly better validation performance.[16,18] The generally weaker associations with measured outdoor concentrations in Barcelona could further be related to the location of the reference site which might have been less representative, the site was situated close to the sea. Moreover the reference site in Barcelona had more missing data (SI2). Consistently, Table S6 in SI2 documents somewhat lower temporal though still high correlations between the reference site and home outdoor measurements. The high sampling height at three high traffic homes in Helsinki has likely contributed to lower performance in the Helsinki data.

LUR Modeled and Measured Indoor and Personal Exposure

The consistent significant associations of the LUR modeled concentrations with personal exposure found for soot and the lack of associations for $PM_{2.5}$ agrees with a previous study in Utrecht comparing personal exposure of elderly adults living near major roads versus minor roads.[19] Van Roosbroeck et al. found no difference in personal NO_2 exposure between adults living in major roads and minor roads.[19] LUR models were not eval-

uated in that study. Similar results have been reported by Sahsuvaroglu et al. (2009) in a study where the 72-hour personal exposure of 33 elderly adults was measured in three seasons.[2] The LUR models, that predict long term concentrations, were compared to short term personal measurements. Predicted NO_2 LUR exposures were not associated with personal NO_2. This could have been influenced by temporal differences in the concentrations. In a study by Nethery et al. 55 pregnant women in Vancouver, Canada completed two to three 48 hour samples. LUR models predicted personal exposure to NO_2 and NO but not to $PM_{2.5}$ and soot.[3] The LUR models for the particle metrics in that study had lower R^2 values than the R^2 values for the ESCAPE models. Low spatial variability was offered as one explanation for the lack of $PM_{2.5}$ association. The soot model in Vancouver largely included traffic variables, whereas personal soot exposures were also affected by vegetative burning as indicated by the significant correlation with levoglucosan.[3] The different findings in our study and the Vancouver study support that validation needs to be conducted locally.

In the current study we evaluated spatial associations between outdoor and personal exposures, relevant for long-term exposure epidemiological studies. There are a large number of studies documenting generally moderate to high correlations between temporal variability of outdoor and personal exposure for $PM_{2.5.}$[20]

Interpretation of Personal Exposure Prediction and Limitations

The stronger correlation between LUR modeled outdoor and measured personal exposure for soot compared to $PM_{2.5}$ is likely due to a combination of higher spatial variability, better infiltration and fewer indoor sources. Furthermore, infiltration is likely to be more efficient for ambient soot than for $PM_{2.5,}$ because soot is generally concentrated in the submicrometer particles of $PM_{2.5}$ which have high penetration and low decay losses.[21-23] Indoor sources are more common for $PM_{2.5}$ than for soot[19] and may have obscured an association for $PM_{2.5}$, despite our efforts to exclude smoking and adjust for other known sources. In a study in four European cities we also observed that limitation to non-smokers was insufficient to exclude indoor source influences on the relationship between outdoor and indoor concentrations for fine and ultrafine concentrations.[8] In a time series study evaluating temporal relationships Sarnat and co-workers[17] reported that due to indoor sources the outdoor concentrations of NO_2 correlated better with measured personal $PM_{2.5}$ than with measured personal NO_2. In our study evaluating spatial contrasts, we found that modeled outdoor $PM_{2.5}$ was more closely associated with measured personal soot than with measured personal $PM_{2.5}$ (SI3). As has been argued in the framework

of time series studies, the relevant correlation is that between outdoor concentrations and the personal exposure to outdoor-origin concentrations, which is difficult to quantify.[17] In our study, the personal soot measurements likely represent personal exposure to outdoor fine particles best and the association found with modeled $PM_{2.5}$ (and NO_2 and NO_x) is therefore reassuring.

The interpretation should further take into account that in each city a relatively small number of subjects was measured and thus we had limited power to detect modest correlations. Only R^2 values above 0.25 (equivalent to a Pearson correlation of 0.5) were significant in the city-specific analyses. Estimated correlation coefficients for $PM_{2.5}$ were non-significant and furthermore very low (between 0.00 and 0.08 for personal exposure), A leave-one out cross-validation analysis, subsequently leaving out one subject from the analysis, found a maximum R^2 of 0.28, 0.17 and 0.06 for $PM_{2.5}$ personal exposure in Utrecht, Helsinki and Barcelona respectively SI9) compared to 0.06, 0.08, and 0.00 for the full set of 15 subjects (Table 3). Consistently, we did find significant associations between modeled and measured concentrations in the pooled dataset, which includes 45 subjects. We performed the study with 15 subjects, because we attempted to characterize the average personal exposure per subject by a relatively large number of measurements (six 96-hour samples), adding up to approximately one year of field work. Personal exposure validation studies for long-term air pollution exposure studies remain challenging.

As observed for the correlation of LUR models with outdoor concentrations, correlations with personal exposure were generally highest in Utrecht and lowest in Barcelona. In addition to the factors related to outdoor prediction discussed before, differences in indoor sources and time activity may explain differences in correlations with indoor and personal exposure. ETS exposure tended to be more frequent in Barcelona, but exclusion of the infrequent reported ETS exposure did not change the correlations substantially (SI8). Barcelona was also the only city with an underground, which was occasionally used by the volunteers. Because of the distribution of sources e.g. gas cooking (reflecting true differences across the cities) it was not possible to account for these factors.

NO_2 and NO_x Associations

Personal NO_2 was associated with modeled outdoor NO_2 in Utrecht and Helsinki but not Barcelona. NO_x LUR models did not, but measured outdoor NO_x did correlate with the personal concentrations in Utrecht and Barcelona. This indicates limited performance of the NO_x models, not reflected in the performance statistics of the models. The weaker associations found for the NO_x compared to NO_2 personal measurements is likely a

reflection of indoor sources. Indoor /outdoor ratios were close to 1 for NO_x and about 0.7 for NO_2 (Table 3). Indoor NO_x concentrations were furthermore highly correlated with personal exposure. The weaker associations between modeled outdoor and measured personal concentrations for NO_2 and NO_x compared to soot, is likely a result of fewer indoor sources and better infiltration for soot.[19] Interestingly, modeled outdoor NO_2 and NO_x were associated with measured personal soot concentrations. As argued for $PM_{2.5}$, if we are interested in NO_2 as a proxy for outdoor combustion sources, the correlation with the (difficult to quantify) personal exposure to NO_2 from outdoor origin is more important than the correlation with total NO_2.

Pooled Analysis

An analysis of the pooled data from the three cities showed highly statistically significant associations between LUR modeled and measured outdoor, indoor and personal concentrations for all pollutants, reflecting the differences in outdoor air pollution between Barcelona, Utrecht and Helsinki. This suggests that over larger ranges of outdoor concentrations, modeled or measured outdoor concentrations are good proxies for personal exposures of soot, NO_2, NO_x and $PM_{2.5}$. This is in agreement with observations from the European EXPOLIS[24] study and the Swiss SAPALDIA study.[25] After adding indicators for city, soot and NO_2 modeled concentrations were still significantly associated with personal exposure, but $PM_{2.5}$ and NO_x not. This suggests that for the latter pollutants the model did not add further explanatory power than a single city background value from between-city analyses. For $PM_{2.5}$ this could be explained by the relatively small contrast within cities compared to between cities. The pooled analysis is relevant for epidemiological studies which include both between and within city exposure contrasts.

References

1. Hoek, G.; Beelen, R.; de Hoogh, K., et al A review of land-use regression models to assess spatial variation of outdoor air pollution. *Atmos. Environ.* **2008,** *42,* 7561-7578.

2. Sahsuvaroglu, T.; Su, J.G.; Brook, J.; Burnett, R.; Loeb, M.; Jerrett, M. Predicting personal nitrogen dioxide exposure in an elderly population: Integrating residential indoor and outdoor measurements, fixed-site ambient pollution concentrations, modeled pollutant levels, and time-activity patterns. *J. Toxicol. Environ. Health Part A Curr. Iss.* **2009,** *72,* 1520-1533.

3. Nethery, E.; Teschke, K.; Brauer, M. Predicting personal exposure of pregnant women to traffic-related air pollutants. *Sci. Total Environ.* **2008,** *395,* 11-22.

4. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric*

Environment **2012,** *62,* 303-317.

5. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. *Environ. Sci. Technol.* **2012,** *46,* 11195-11205.

6. Cyrys, J.; Eeftens, M.; Heinrich, J., et al Variation of NO2 and NOx concentrations between and within 36 European study areas: Results from the ESCAPE study. *Atmos. Environ.* **2012,** *62,* 374-390.

7. Avery, C.L.; Mills, K.T.; Williams, R., et al Estimating error in using ambient PM2.5 concentrations as proxies for personal exposures: A review. *Epidemiology* **2010,** *21,* 215-223.

8. Hoek, G.; Kos, G.; Harrison, R., et al Indoor-outdoor relationships of particle number and mass in four European cities. *Atmos. Environ.* **2008,** *42,* 156-169.

9. ISO Ambient air- determination of a black smoke Index. **1993,** *ISO 9835,*

10. Cyrys, J.; Heinrich, J.; Hoek, G., et al Comparison between different traffic-related particle indicators: elemental carbon (EC), PM2.5 mass, and absorbance. *J. Expo. Anal. Environ. Epidemiol.* **2003,** *13,* 134-143.

11. Janssen, N.A.H.; Van Vliet, P.H.N.; Aarts, F.; Harssema, H.; Brunekreef, B. Assessment of exposure to traffic related air pollution of children attending schools near motorways. *Atmos. Environ.* **2001,** *35,* 3875-3884.

12. Brunekreef, B.; Janssen, N.A.; de Hartog, J.J., et al Personal, indoor, and outdoor exposures to PM2.5 and its components for groups of cardiovascular patients in Amsterdam and Helsinki. *Res. Rep. Health Eff. Inst.* **2005,** 1-70; discussion 71-79.

13. Van Roosbroeck, S.; Jacobs, J.; Janssen, N.A.H.; Oldenwening, M.; Hoek, G.; Brunekreef, B. Long-term personal exposure to PM2.5, soot and NOx in children attending schools located near busy roads, a validation study. *Atmos. Environ.* **2007,** *41,* 3381-3394.

14. Eeftens, M.; Beelen, R.; Fischer, P.; Brunekreef, B.; Meliefste, K.; Hoek, G. Stability of measured and modelled spatial contrasts in NO 2 over time. *Occup. Environ. Med.* **2011,** *68,* 765-770.

15. Beelen, R.; Hoek, G.; Vienneau, D., et al Development of NO2 and NOx land use regression models for estimating air pollution exposure in 36 study areas in Europe - The ESCAPE project. *Atmos. Environ.* **2013,** *72,* 10-23.

16. Wang, M.; Beelen, R.; Eeftens, M.; Meliefste, K.; Hoek, G.; Brunekreef, B. Systematic evaluation of land use regression models for NO 2. *Environ. Sci. Technol.* **2012,** *46,* 4481-4489.

17. Sarnat, J.A.; Brown, K.W.; Schwartz, J.; Coull, B.A.; Koutrakis, P. Ambient gas concentrations and personal particulate matter exposures: Implications for studying the health effects of particles. *Epidemiology* **2005,** *16,* 385-395.

18. Basagaña, X.; Rivera, M.; Aguilera, I., et al Effect of the number of measurement sites on land use regression models in estimating local air pollution. *Atmos. Environ.* **2012,** *54,* 634-642.

19. Van Roosbroeck, S.; Hoek, G.; Meliefste, K.; Janssen, N.A.H.; Brunekreef, B. Validity of residential traffic intensity as an estimate of long-term personal exposure to traffic-related air pollution among adults. *Environmental Science and Technology* **2008,** *42,* 1337-1344.

20. Wallace, L. Correlations of Personal Exposure to Particles with Outdoor Air Measurements: A Review of Recent Studies. *Aerosol Science and Technology* **2000,** *32,* 15-25.

21. Sarnat, S.E.; Coull, B.A.; Ruiz, P.A.; Koutrakis, P.; Suh, H.H. The influences of ambient particle composition and size on particle infiltration in Los Angeles, CA, residences. *J. Air Waste Manag. Assoc.* **2006,** *56,* 186-196.

22. Abt, E.; Suh, H.H.; Catalano, P.; Koutrakis, P. Relative Contribution of Outdoor and Indoor Particle Sources to Indoor Concentrations. *Environ. Sci. Technol.* **2000,** *34,* 3579-3587.

23. Long, C.M.; Suh, H.H.; Catalano, P.J.; Koutrakis, P. Using time- and size-resolved particulate data to quantify indoor penetration and deposition behavior. *Environ. Sci. Technol.* **2001,** *35,* 2089-2099.

24. Georgoulis, L.B.a.; Hänninen, O.b.; Samoli, E.a., et al Personal carbon monoxide exposure in five European cities and its determinants. *Atmos. Environ.* **2002,** *36,* 963-974.

25. Monn, C.; Brändli, O.; Schindler, C.; Ackermann-Liebrich, U.; Leuenberger, P. Personal exposure to nitrogen dioxide in Switzerland. *Sci. Total Environ.* **1998,** *215,* 243-251.

Supplemental Information

LUR models

Table S1 ESCAPE Land Use Regression models for PM2.5 and Soot (Eeftens et al. 2012)

Study area	LUR model[1]	R^2 of model	R^2 validation	RMSE[2] (validation) ($\mu g/m^3$)	Number of sites[3]	Measured concentration ($\mu g/m^3$)[4]
$PM_{2.5}$						
Helsinki/ Turku, Finland	9.25 – 6.75E-6*NATURAL_500[4] + 6.34E-7*TRAFMAJOR-LOAD_50	67%	53%	1.0	20	8.6 [5.3 – 12.3]
Netherlands/ Belgium	9.46 + 0.42*REGIONALESTIMATE + 0.01*MAJOR-ROADLENGTH_50 + 2.28E-9*TRAFMAJORLOAD_1000	67%	61%	1.2	40	17.7 [12.7 – 21.5]
Barcelona, Spain	16.21 – 4.08E-6*GREEN_1000 + 2.04E-7*TRAFLOAD_100 + 6.82E-3*INTINVDIST2	83%	71%	2.1	20	16.3 [8.4 – 24.4]
Soot						
Helsinki/ Turku, Finland	1.15 + 2.09E-7*TRAFLOAD_50 – 1.15E-6*NATURAL_500[4]	65%	47%	0.3	20	1.1 [0.6 – 2.3]
Netherlands/ Belgium	0.07 + 2.95E-9*TRAFLOAD_500 + 2.93E-3*MAJOR-ROADLENGTH_50 + 0.85*REGIONALESTIMATE + 7.90E-9*HLDRES_5000 + 1.72E-6*HEAVYTRAFLOAD_50	92%	89%	0.2	40	1.7 [0.9 – 3.0]
Barcelona, Spain	1.01 + 7.46E-6*HDRES_300 + 2.66E-3*INTINVDIST2 + 1.11E-7**TRAFLOAD_50	86%	80%	0.4	20	2.7 [0.9 – 4.9]

1 Most variables are buffers with _xxx indicating the size of the buffer in m (e.g. HHOLD_500 is the number of households in a 500m buffer). TRAFLOAD is traffic intensity * length of road in a buffer. HDRES and LDRES are high and low density residential land use. INTINVDIST is product of traffic intensity and inverse distance to the nearest road. SQRALT is square root of altitude. Major road as road classes 0, 1 and 2 (motorways, main roads of major importance and other main roads) from the central road network or roads with more than 5,000 vehicles/day based upon local networks with linked traffic intensity. INTINVDIST is traffic intensity multiplied by inverse distance (squared).
2 RMSE is the root mean square error, which can be interpreted as the "average" residual (difference between observed and modeled concentration). 3 Number of sites that have been used for model development. 4 Mean [min - max]. Units are $10^{-5} m^{-1}$ for soot.

Table S2 ESCAPE Land Use Regression models for NO_2 and NO_x (Beelen et al. 2013)

Study area	LUR model [1]	R^2 of model	R^2 validation	RMSE[2] (validation) ($\mu g/m^3$)	Number of sites[3]	Measured concentration ($\mu g/m^3$) [4]
NO_2						
Helsinki and Turku, Finland	7.61 + 1.18E-5*TRAFLOAD_25 + 3.43E-8*TRAFLOAD_25_1000 + 0.04*ROADLENGTH_25 + 1.24E-3*ROADLENGTH_25_300 – 9.18E-5*URBGREEN_5004	83%	75%	3.4	40	18.9 [6.1 – 40.8]
Netherlands and Belgium	-7.80 + 1.18*REGIONALESTIMATE + 2.30E-5*POP_5000 + 2.46E-6*TRAFLOAD_50 + 1.06E-4*ROADLENGTH_1000 + 9.84E-5*HEAVYTRAFLOAD_25 + 12.19*DISTINVNEARC1 + 4.47E-7*HEAVYTRAFLOAD_25_500	86%	81%	5.1	80	30.9 [12.8 – 61.5]
Barcelona, Spain	3.16 + 6.26E-3*INTINVDIST1 + 1.18E-4*HDRES_300 + 992.09*DISTINVMAJOR2 + 3.51E-4*ROADLENGTH_1000	75%	68%	11.6	40	57.7 [13.8 – 109.0]
NO_x						
Helsinki and Turku, Finland	12.56 + 3.46E-5*TRAFLOAD_25 + 4.92E-8*TRAFLOAD_25_1000 + 1.70E-2*ROADLENGTH_100 – 5.58E-5*URBGREEN_10004 + 2.54E-3*HHOLD_300	85%	74%	7.8	40	30.6 [8.6 – 94.7]
Netherlands and Belgium	3.25 + 0.74*REGIONALESTIMATE + 4.22E-6*TRAFLOAD_50 + 6.36E-4*POP_1000 + 2.39E-6*HEAVYTRAFLOAD_500 + 71.65*DISTINVMAJOR1 + 0.21*MAJORROADLENGTH_25	87%	82%	11.2	80	51.8 [17.5 – 130.8]
Barcelona, Spain	32.85 + 2.55E-4*HDRES_300 + 2815.14*DISTINVMAJOR2 + 3.87E-5*TRAFLOAD_25	73%	65%	27.7	40	101.3 [21.0 – 236.4]

1 Most variables are buffers with _xxx indicating the size of the buffer in m (e.g. HHOLD_500 is the number of households in a 500m buffer). TRAFLOAD is traffic intensity*length of road in a buffer. HDRES and LDRES are high and low density residential land use. INTINVDIST is product of traffic intensity and inverse distance to the nearest road. SQRALT is square root of altitude. Major road as road classes 0, 1 and 2 (motorways, main roads of major importance and other main roads) from the central road network or roads with more than 5,000 vehicles/day based upon local networks with linked traffic intensity. INTINVDIST is traffic intensity multiplied by inverse distance (squared). DISTINVMAJOR is inverse distance to a major road.
2 RMSE is the root mean square error, which can be interpreted as the "average" residual (difference between observed and modeled concentration) 3 Number of sites that have been used for model development. 4 Mean [min - max]

Temporal adjustment

In the Netherlands, measurements were done in 32 weeks (2 extra weeks were scheduled to replace some missing data). During two of these measuring weeks, data from the reference site were missing because of technical failure. In Spain, the number of measuring weeks was 30. Out of these 30 weeks, 7 had missing data at the reference site. Four missing measurements occurred because no units were available and three because of technical failure.

For the missing measurements on the reference site in Spain and the Netherlands, imputation was applied. The measurements on the reference site were compared to measurements at fixed monitoring sites from the RIVM ('Rijksinstituut voor Volksgezondheid en Milieu', the National institute for Public Health and the Environment) in the Netherlands and the National Network in Barcelona (Gencat, Generalitat de Catalunya). The regression formula comparing the VE^{3}SPA reference site with the fixed site was used to calculate the concentrations for the missing data (Table S3).

Table S3 Formula's for the imputation of missing values on the reference site.

City	Comp	Independent component, site	n	α	β	Formula[1]	R^2
Utrecht	Soot	BS, 738	28	0,27	0,12	Vref=0.27+0.12*F	0,70
	$PM_{2.5}$	$PM_{2.5}$, 633	29	-3,78	0,78	Vref=-3,78+0,78*F	0,69
	NO_2	NO_2, 738	30	5,82	0,95	Vref=5,82+0,95*F	0,61
	NO_x	NO_x, 738	30	1,73	1,51	Vref=1,73+1,51*F	0,73
Barcelona	$PM_{2.5}$	PM_{10}, Verdaguer	20	-10,08	0,85	Vref=-10,08+0,85*F	0,66
	Soot	NO_x, Hospitalet	22	-0,06	0,03	Vref=-0,06+0,03*F	0,61
	NO_2	NO_2, Hospitalet	24	-0,16	1,21	Vref=-0,16+1,21*F	0,64
	NO_x	NO_x, Hospitalet	24	6,96	1,26	Vref=6,96+1,26*F	0,71

The imputed component (comp) and the independent component with the name or number of the fixed monitor site, the number of measurements in the linear regression (n), the intercept (α), the Beta (β) and the R^2 are given and entered in the imputation formula. Note: Black Smoke and soot are different methods for Black Carbon determination.

1 Vref is the VE3SPA reference site and F is the fixed reference site

In the Netherlands, the R^2 of soot on the VE^{3}SPA reference site compared to black smoke on site 738 of the RIVM was 0.70. NO_2 and NOx also correlated best with site 738 and had a R^2 of 0.61 and 0.73 respective-

ly. For $PM_{2.5}$ the best correlation (R^2=0.69) was with the PM_{10} concentration on site 633 of the RIVM. In Spain, the VE³SPA $PM_{2.5}$ concentrations at the reference site correlated with a R^2 of 0.66 with the PM_{10} (better than with $PM_{2.5}$) measured at the IES Verdaguer site (Gencat). The NO_2 concentration at Hospitalet was used for the imputation of NO_2, the R^2 was 0.64. For NO_x the concentrations of NO_2 and NO at the Hospitalet site were combined. This correlated with an R^2 of 0.75 with the VE³SPA NOx measurements. The NO_x concentrations were also used for the imputation of soot because soot was not available in the network, the R^2 was 0.61.

Table S4 The median slopes (β) per country of the within person (or temporal) relation between the outdoor measurements and the personal/indoor measurements.

	Helsinki		Utrecht		Barcelona	
Component	indoor	personal	indoor	personal	indoor	personal
$PM_{2.5}$	0.38	0.60	0.41	0.44	0.59	0.64
Soot	0.49	0.42	0.68	0.66	0.62	0.40
NO_2	0.11	0.35	0.29	0.37	0.20	0.25
NOx	0.65	0.80	0.44	0.75	0.88	0.60

The median slopes that were used for the temporal adjustment of the indoor and personal measurements per country are shown (Table S4). The slopes were consistent across the three countries and were all smaller than 1. This makes the influence of the adjustment with the reference site less, which is plausible for the indoor and personal measurements. The median correlation coefficients (R) of these regressions are shown in Table S5.

Table S5 The median correlation coefficients (R) of the association between the home outdoor measurements and the personal/indoor measurements per participant, per city

	Helsinki		Utrecht		Barcelona	
Component	indoor	personal	indoor	personal	indoor	personal
$PM_{2.5}$	0.51	0.67	0.82	0.71	0.79	0.41
Soot	0.79	0.72	0.95	0.89	0.81	0.67
NO_2	0.25	0.77	0.57	0.77	0.48	0.43
NOx	0.85	0.91	0.84	0.85	0.95	0.86

*All correlation coefficients were statistically significant ($p<0.05$)

After imputing the missing measurements at the reference site, the measurements at the reference site were plotted against the outdoor

measurements per participant to show the temporal association of the measurements at the reference site and the outdoor concentrations at the participant address. The median correlation coefficients are shown in Table S6. For most of the volunteers in the three countries, the reference site was well able to predict the temporal fluctuation of the outdoor measurements at the home addresses, the median correlation coefficients in Finland and the Netherlands were very good. This supports the use of the reference site to correct for temporal variability. In Spain, the median correlation coefficients were lower for especially soot and $PM_{2.5}$, but still good. If only the non-imputed measurements at the reference site are plotted, the median correlation coefficients for Spain are a bit higher for soot (0.78) and lower (0.73) for $PM_{2.5}$. This indicates that the reference site in Spain was less predictive for the temporal fluctuations at the sites, which was not explained by the larger number of imputed values.

Table S6 Median correlation coefficients (R) of the outdoor measurements versus the measurements at the reference site (including the imputed values) per ID

Component	Helsinki	Utrecht	Barcelona
$PM_{2.5}$	0.88	0.92	0.79
Soot	0.90	0.88	0.72
NO_2	0.97	0.92	0.89
NOx	0.85	0.93	0.86

The corrected mean concentrations correlated well with the uncorrected mean of the measurements (Table S7). The correlation of the corrected and uncorrected mean was less for $PM_{2.5}$ than for the other components, as observed in the ESCAPE project.[1,2] This was explained by the authors by the observation that the measured $PM_{2.5}$ concentration had lower seasonal variability and were more dependent on the weather, resulting in larger within season variability. Therefore the uncorrected mean could deviate more from the corrected mean.[1] The outdoor corrected measurements had lower correlations with the uncorrected measurements than the indoor and personal measurements. This was a result of the procedure in which for the outdoor measurements we directly subtracted the differences at the reference site, while we used the difference multiplied by an indoor/outdoor slope (<1) for the indoor and personal measurements.

Modeled $PM_{2.5}$, NO_2, NO_x and measured personal soot

In Table S8 the associations of the measured soot concentrations with the modeled personal $PM_{2.5}$, NO_2 and NO_x concentrations are shown. Associations are usually stronger than with the personal exposure of the component itself.

Table S7 The correlation (R^2) of the corrected mean versus the uncorrected mean concentrations.

$PM_{2.5}$	outdoor	indoor	personal
Utrecht	0.40	0.96	0.85
Helsinki	0.26	0.99	0.86
Barcelona	0.41	0.77	0.85
Soot	**outdoor**	**indoor**	**personal**
Utrecht	0.93	0.89	0.81
Helsinki	0.81	0.99	0.98
Barcelona	0.69	0.81	0.87
NO_2	outdoor	indoor	personal
Utrecht	0.95	0.99	0.97
Helsinki	0.81	1.00	0.98
Barcelona	0.88	0.99	0.97
NO_x	outdoor	indoor	personal
Utrecht	0.96	1.00	0.97
Helsinki	0.82	0.99	0.98
Barcelona	0.91	0.85	0.87

Table S8 The coefficient of determination (R^2), the regression coefficient (β), the intercept (α) and the p-value (p) of the regression analysis of the ESCAPE measured soot concentrations versus the mean modeled $PM_{2.5}$, NO_2 and NO_x concentrations.

		Helsinki		
Model	**R^2**	**β**	**α**	**p**
$PM_{2.5}$	0.29	0.29	-1.68	0.04
NO_2	0.47	0.04	0.01	0.00
NO_x	0.49	0.02	0.16	0.00
		Utrecht		
Model	**R^2**	**β**	**α**	**p**
$PM_{2.5}$	0.32	0.09	-0.44	0.03
NO_2	0.60	0.02	0.46	0.00
NO_x	0.55	0.01	0.61	0.00
		Barcelona		
Model	**R^2**	**β**	**α**	**p**
$PM_{2.5}$	0.00	0.01	2.00	0.81
NO_2	0.16	0.01	1.42	0.15
NO_x	0.21	0.00	1.64	0.08

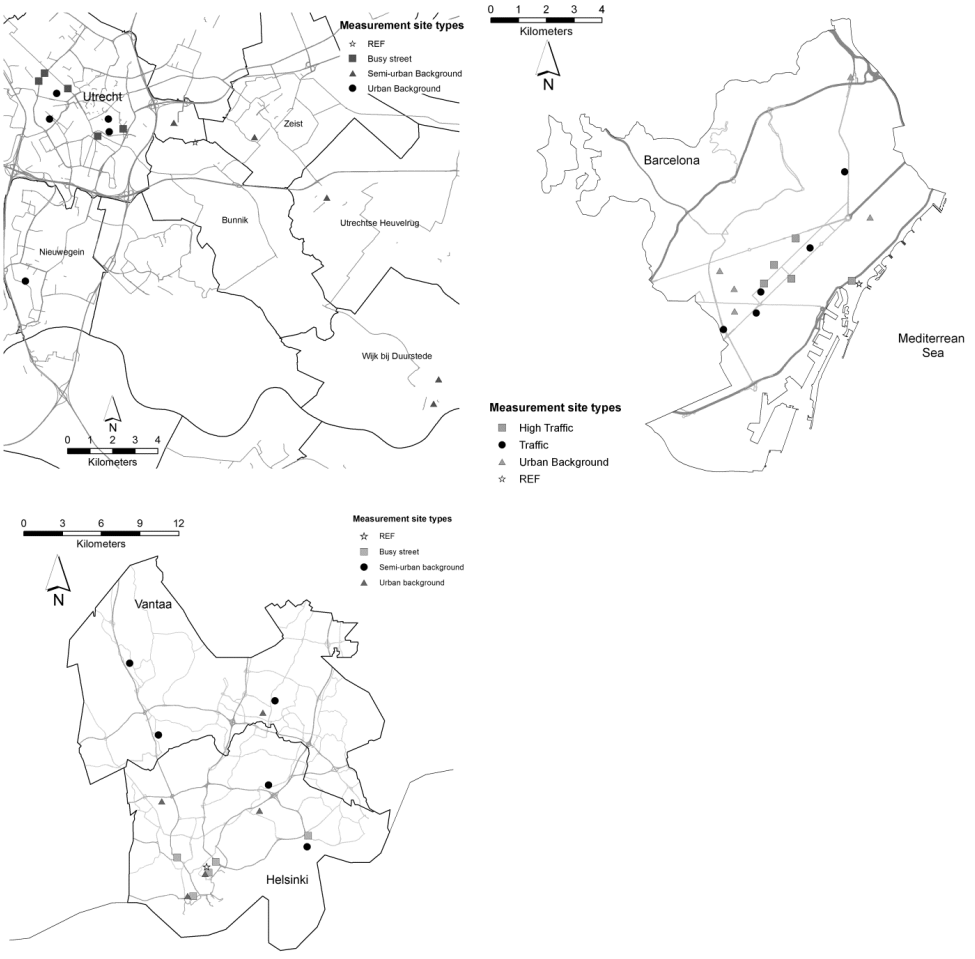
Site description

Table S9 Distribution of home characteristics

		Utrecht	Barcelona	Helsinki
Traffic intensity (veh.day^{-1})*	Traffic site	16805 (5066)	21722 (9840)	18675(13886)
	Urban background	1511 (1660)	10254 (7386)	1053 (747)
	Semi-urban background	542 (453)	1040 (721)	867 (1770)
Sampling height (m)*	Traffic site	3.3 (7.2)	5.2 (4.1)	15.4 (9.2)
	Urban background	4.3 (0.8)	6.4 (3.4)	10.8 (6.6)
	Semi-urban background	4.4 (3.3)	9.4 (4.9)	2.4 (1.4)
House type	Detached family home	0	0	2
	Attached family home	11	0	2
	Flat/apartment	4	15	11
Home volume	<100 m^3	0	3	3
	100-200 m^3	6	8	6
	200-300 m^3	5	2	4
	>300 m^3	4	2	2
Built	1800-1944	8	3	2
	1945-1979	5	10	8
	>1980	2	2	5
Type kitchen is open (n (%))		9 (60)	0 (0)	6 (40)
Air conditioning (n)		1 (6.7)	8 (53)	0 (0)
Heating	Central in home	11	2	1
	District	1	0	11
	Separate gas/oil heaters	3	6	0
	Electric	0	4	3
	No heating	0	3	0
Cooking on gas (n %)		12 (80)	14 (93)	1 (6.7)
Living room on	Ground level	6	0	6
	First floor	6	8	3
	>2nd floor	3	7	6
Fume hood	No fume hood	5	5	3
	Exhaust air recirculated	2	0	3
	With external vent (*n* (%))	8	10	9
Pet in home	Cat	6	0	3
	Dog	4	1	3
	Other	5	1	1
Floor cover	Smooth	9	10	6
	Carpet	2	4	0
	Rug (larger than 1 m^3)	4	1	9

* Mean (standard deviation). Traffic counted manually (van Roosbroeck, 2007)

Figure S1 Maps of the VE3SPA sites in Helsinki (top left), Barcelona (top right) and Utrecht (bottom left).



Quality assurance, quality control

Table S10 describes the results of the field blanks that were collected. Overall, the field blanks were low, although there were a few blank $PM_{2.5}$ measurements that had quite high negative values. It could be that while transporting the filters to the filter cassette, a small part of the support filter was shipped of. This was not noted by the field worker and thus the blank was still included in the analyses.
The soot measurements were all above the detection limit (DL), most $PM_{2.5}$ and NO_2 as well (Table S11).

Table S10 Field blanks and detection limit for $PM_{2.5}$ (µg/m³), soot reflectance ($10^{-5}m^{-1}$), NO_2 and NO (µg/m³)

	N field blanks		Average field blank				Detection limit			
Study area	$PM_{2.5}$	NO_x	$PM_{2.5}$	Soot*	NO_2	NO_x	$PM_{2.5}$	Soot	NO_2	NO_x
Utrecht	15	13	0.00	102.7	-.01	-0,99	1.22	0.12	2,1	12,0
Helsinki	16	17	0.00	101.9	0.51	1,24	2.35**	0.11	5,8	5,8
Barcelona	15	13	0,01	102.3	0.54	1,75	5.17†	0.13	1,9	4,3

*this is the R0 in the formula for the absorption coefficient that can be found on page 11.
** When the sample of S13 8-10-2010 (filter 10756) was excluded, the detection limit was 1.15 µg/m³
† When the sample of F113 at 6-12-2010 (filter 10534) was excluded, the detection limit was 0.73 µg/m³

Table S11 Number of included samples below the detection limit.

	measurements (n)			
Study area	$PM_{2.5}$	Soot	NO_2	NO_x
Utrecht	1	0	0	7
Helsinki	16*	0	5	8
Barcelona	8*	0	1	0

* When the Blank filters 10756 and 10534 were excluded from the detection limit calculations, none of the filters were below detection limit.

Table S12 Duplicate measurements

	n duplicates		CV (%)			
Outdoor/Indoor Duplicates						
Study area	$PM_{2.5}$/ soot	NO_x	$PM_{2.5}$	Soot	NO_2	NO_x
Utrecht	13	17	21,6%	11,1%	9,0%	10,2%
Helsinki	15	14	11,5%	12,6%	9,0%	8,3%
Barcelona	15	5	9,2%	6,8%	20,3%	5,7%
Personal Duplicates						
Utrecht	4	5	7,7%*	21,8%*	4,7%	3,0%
Helsinki	5	5	9,2%	7,5%	6,6%	26,7%†
Barcelona	5	3	40,8%**	27,6%	4,4%	7,4%

*if we don't include volunteer N16, the Dutch CV would be 2.31% for $PM_{2.5}$ and 7.10% for Soot.
** If we don't include the personal duplicate measurement of volunteer S19 than the CV would be 23,65% for $PM_{2.5}$
†9.1% if not including volunteer F994

The measurements that were below the detection limit are nonetheless included in the analysis. Finland had the most measurements under the detection limit, because of the overall low concentrations in Finland (section 6.2.6).
The results of the duplicate measurements are described in Table S12. Most coefficients of variation are about 10% which is acceptable. The CV for $PM_{2.5}$ is larger for the Netherlands than for Finland and Spain. For some of the duplicate measurements a pump unit was used that had given some technical problems in the past. The best units were used for the actual measurements. The coefficient of variance (CV) for $PM_{2.5}$ of 21.63% in the Netherlands thus likely gives an upper estimate of the uncertainty. A CV value of 10% in individual measurements translates into a CV of the average (based upon six measurements) of about 4% (10% / √6). A CV value of 20% in individual measurements translates into a CV of the average (based upon six measurements) of about 8% (20% / √6). Because of the small number of personal duplicates for $PM_{2.5}$, soot and NO_2, these CV values are less interpretable.

Scatterplots modeled versus measured concentrations

Figure S2 Regression plots of the corrected measured average versus modeled concentration for NO_2 and NO_x in Utrecht, Helsinki and Barcelona

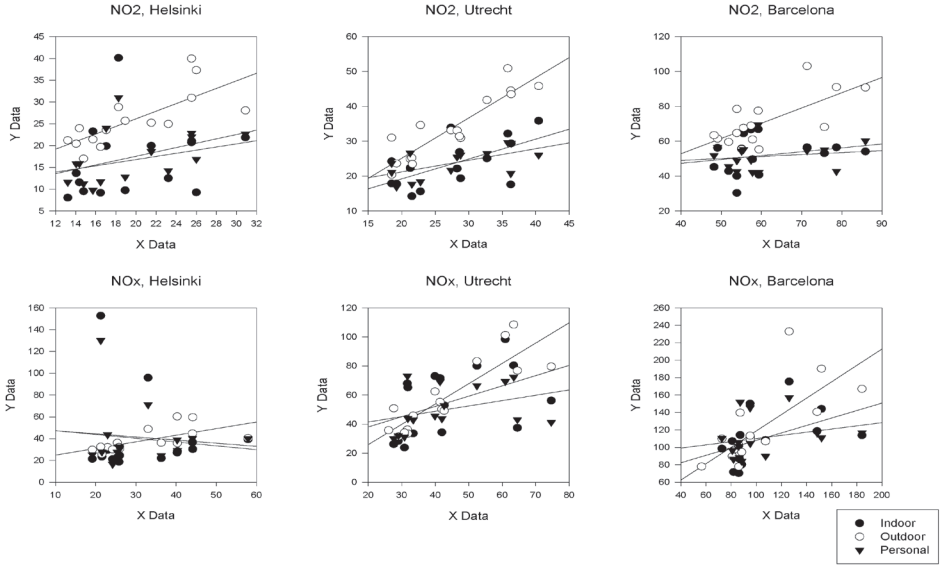
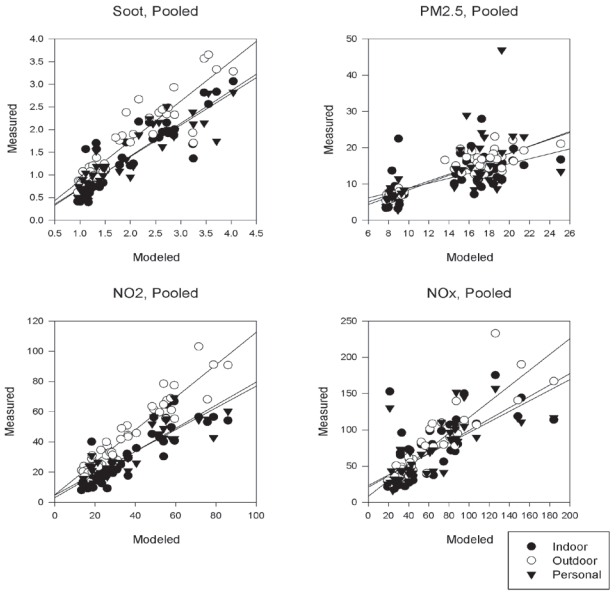


Figure S3 Regression of the pooled data set of the three countries.



Associations of modeled and measured concentrations using an alternative adjustment method for temporal variation

When the concentrations were corrected by including the measurements at the reference site in the model, the results were comparable with the absolute differences correction method (Table S13). The p-values for the modeled concentrations (pm) show the probability that adding the modeled concentrations in the regression model is significant. With this method, the outdoor NO_x in Finland is not significant anymore. Also with the reference site included in the model, we see that the models significantly predict the outdoor concentrations of soot, NO_2 and NO_x in the three countries. Table S13 shows that the indoor NO_x for the Netherlands and Spain was significant when including the reference site in the model. With the absolute differences method, these associations were borderline significant. No associations were found with personal exposure.

Table S13 The coefficient of determination (R^2), the regression coefficient of the reference site (βr) the regression coefficient of the modeled concentrations (βm) and the intercept (α) of the regression analysis of the ESCAPE modeled concentrations versus the mean measured VE³SPA concentrations, with the measurements at the reference site included in the model

$PM_{2.5}$	Outdoor				Indoor				Personal			
City	R^2	βr	βm	α	R^2	Br	βm	α	R^2	βr	βm	α
Utrecht	0.66	0.86*	1.08*	-13.88	0.57	1.37*	0.32	-10.94	0.35	0.62*	-0.39	10.12
Helsinki	0.78	0.93*	0.61	-4.88	0.23	1.44	1.34	-14.08	0.21	0.46	1.14	-6.61
Barcelona	0.57	0.84*	0.23	-0.79	0.06	0.27	0.00	11.84	0.06	0.64	-0.34	18.43
Soot	**Outdoor**				**Indoor**				**Personal**			
City	R^2	Br	Bm	α	R^2	Br	Bm	α	R^2	R^2	βr	βm
Utrecht	0.83	1.60*	1.16*	-1.92	0.81	1.39*	0.65*	-1.24	0.68	1.03*	0.37*	-0.48
Helsinki	0.60	1.26*	0.94*	-1.22	0.41	1.84	1.93*	-2.99	0.47	1.13	1.45*	-1.86
Barcelona	0.67	-0.02	0.90*	0.01	0.61	-0.07	0.72*	0.16	0.49	0.53†	0.28	0.38
NO_2	Outdoor				Indoor				Personal			
City	R^2	Br	Bm	α	R^2	Br	Bm	α	R^2	R^2	Br	βm
Utrecht	0.89	1.84*	1.08*	-39.08	0.57	1.38*	0.52*	-23.28	0.58	1.01*	0.30*	-8.45
Helsinki	0.51	0.87	0.80*	-14.60	0.09	0.59	0.31	-5.78	0.28	0.58	0.47	-7.81
Barcelona	0.67	-0.23	1.05*	20.27	0.11	0.45	0.19	16.85	0.10	-0.36	0.20	58.37
NO_x	Outdoor				Indoor				Personal			
City	R^2	Br	Bm	α	R^2	Br	Bm	α	R^2	R^2	Br	βm
Utrecht	0.87	2.49*	1.36*	-89.87	0.76	3.67*	0.61*	-104.27	0.65	2.63*	0.30	-57.34
Helsinki	0.41	1.28†	0.49†	-28.28	0.11	2.54	-0.31	-48.15	0.13	2.09	-0.28	-30.44
Barcelona	0.58	0.12	1.01*	9.67	0.31	0.22	0.48†	43.59	0.14	-0.22	0.25	104.39

Concentrations are corrected for weather differences using the inclusion of the reference site in the regression analysis method. βr reflects temporal variation. Bm the spatial component. The R^2 cannot be compared with Table 4 from the main paper.

* Significant at the $p<0.05$ level † Significant at the $p<0.10$ level

P values Table S13

$PM_{2.5}$	Outdoor		Indoor		Personal	
City	pr	pm	pr	pm	pr	pm
Utrecht	0.002	0.011	0.002	0.589	0.037	0.394
Helsinki	0.000	0.182	0.131	0.584	0.274	0.315
Barcelona	0.002	0.380	0.393	0.996	0.435	0.707
Soot	**Outdoor**		**Indoor**		**Personal**	
City	pr	pm	pr	pm	pr	pm
Utrecht	0.004	0.000	0.001	0.000	0.004	0.008
Helsinki	0.011	0.007	0.120	0.026	0.136	0.012
Barcelona	0.946	0.001	0.799	0.002	0.060	0.136
NO_2	Outdoor		Indoor		Personal	
City	pr	pm	pr	pm	pr	pm
Utrecht	0.001	0.000	0.030	0.017	0.015	0.026
Helsinki	0.153	0.018	0.510	0.500	0.333	0.132
Barcelona	0.646	0.000	0.474	0.501	0.424	0.310
NO_x	Outdoor		Indoor		Personal	
City	pr	pm	pr	pm	pr	pm
Utrecht	0.000	0.000	0.000	0.027	0.001	0.179
Helsinki	0.055	0.071	0.263	0.734	0.233	0.691
Barcelona	0.858	0.002	0.690	0.052	0.637	0.201

Environmental Tobacco Smoke

Table S14 Regression analyses of the modeled outdoor versus the measured indoor/personal concentrations, the measurements with environmental tobacco smoke (ETS) are excluded from analysis. Only participants with more than one measurement are included.

ETS excluded from analyses										
$PM_{2.5}$	**Indoor**					**Personal**				
City	N	R^2	β	α	p	N	R^2	β	α	p
Utrecht	15	0.01	0.31	6.74	0.67	15	0.07	-0.39	18.18	0.35
Helsinki	15	0.04	1.90	-8.36	0.45	15	0.03	0.85	-0.58	0.51
Barcelona	13	0.00	0.08	14.96	0.86	13	0.01	-0.31	28.26	0.76
Soot	**Indoor**					**Personal**				
City	**N**	**R^2**	**β**	**α**	**p**	**N**	**R^2**	**β**	**α**	**p**
Utrecht	15	0.64	0.63	0.10	0.00	15	0.42	0.35	0.50	0.01
Helsinki	15	0.30	1.83	-1.29	0.04	15	0.38	1.34	-0.75	0.01
Barcelona	13	0.35	0.49	0.69	0.03	13	0.14	0.25	1.42	0.21
NO_2	**Indoor**					**Personal**				
City	**N**	**R^2**	**β**	**α**	**p**	**N**	**R^2**	**β**	**α**	**p**
Utrecht	15	0.34	0.56	8.22	0.02	15	0.27	0.27	16.09	0.05
Helsinki	15	0.02	0.23	13.16	0.65	15	0.18	0.49	7.60	0.12
Barcelona	15	0.11	0.32	31.27	0.23	15	0.03	0.14	42.81	0.54
NO_x	**Indoor**					**Personal**				
City	**N**	**R^2**	**β**	**α**	**p**	**N**	**R^2**	**β**	**α**	**p**
Utrecht	15	0.12	0.53	30.80	0.21	15	0.05	0.23	39.32	0.42
Helsinki	15	0.01	-0.33	50.54	0.72	15	0.01	-0.25	48.74	0.72
Barcelona	15	0.17	0.40	67.87	0.13	15	0.01	0.10	101.20	0.67

The number of participants included in the analysis (N), the coefficient of determination (R^2), the regression coefficient (β), the intercept (α) and the p-value (p) of the model.

Leave one out cross-validation

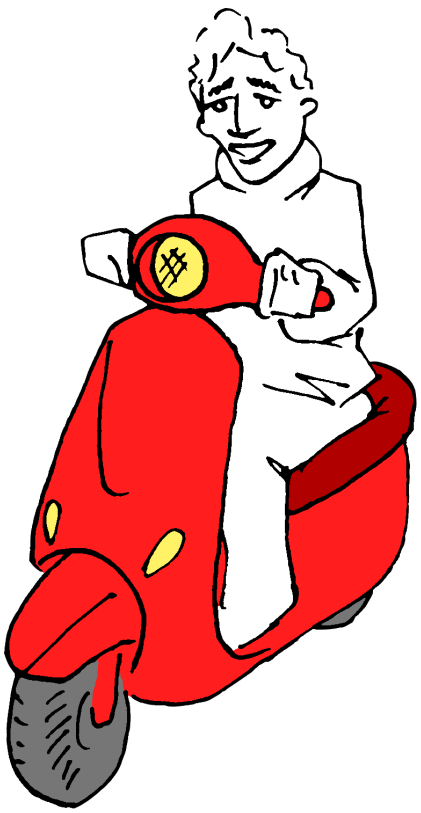
Table S15 The minimum (MIN), maximum (MAX) and standard deviation (STD) of the R squares derived from the leave one out cross validation. N=15, for the 15 models where N-1=14 participants.

		Outdoor			
		Soot	**$PM_{2.5}$**	**NO_2**	**NO_x**
Helsinki	MIN	0.50	0.12	0.50	0.36
	MAX	0.68	0.28	0.71	0.62
	MEAN	0.57	0.21	0.56	0.42
	STD	0.04	0.05	0.05	0.06
Utrecht	MIN	0.72	0.37	0.79	0.72
	MAX	0.80	0.54	0.87	0.83
	MEAN	0.75	0.43	0.82	0.75
	STD	0.02	0.05	0.02	0.03
Barcelona	MIN	0.26	0.02	0.41	0.42
	MAX	0.49	0.17	0.60	0.68
	MEAN	0.33	0.10	0.49	0.51
	STD	0.06	0.04	0.05	0.06
		Personal			
		Soot	**$PM_{2.5}$**	**NO_2**	**NO_x**
Utrecht	MIN	0.37	0.01	0.28	0.07
	MAX	0.61	0.28	0.50	0.30
	MEAN	0.44	0.07	0.35	0.14
	STD	0.06	0.06	0.06	0.07
Barcelona	MIN	0.05	0.00	0.00	0.04
	MAX	0.42	0.06	0.12	0.14
	MEAN	0.20	0.01	0.03	0.07
	STD	0.08	0.02	0.03	0.03
Helsinki	MIN	0.28	0.03	0.15	0.01
	MAX	0.45	0.17	0.40	0.08
	MEAN	0.39	0.08	0.21	0.02
	STD	0.05	0.04	0.06	0.02

References

1. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric Environment* **2012,** *62,* 303-317.

2. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. *Environ. Sci. Technol.* **2012,** *46,* 11195-11205.



Chapter 3

The association of LUR modeled $PM_{2.5}$ elemental composition with personal exposure

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Abstract

Background and aims Land use regression (LUR) models predict spatial variation of ambient concentrations, but little is known about the validity in predicting personal exposures. In this study, the association of LUR modeled concentrations of $PM_{2.5}$ components with measured personal concentrations was determined. The elements of interest were copper (Cu), iron (Fe), potassium (K), nickel (Ni), sulfur (S), silicon (Si), vanadium (V) and zinc (Zn).

Methods In Helsinki (Finland), Utrecht (the Netherlands) and Barcelona (Spain) five participants from urban background, five from suburban background and five from busy street sites were selected in each city (15 participants per city). Outdoor, indoor and personal 96-hour $PM_{2.5}$ samples were collected by the participants over periods of two weeks in three different seasons (winter, summer and spring/autumn) and the overall average was calculated. Elemental composition was measured by ED-XRF spectrometry. The LUR models for the average ambient concentrations of each element were developed by the ESCAPE project.

Results LUR models predicted the within-city variation of average outdoor Cu and Fe concentrations moderately well (range in R^2 27-67% for Cu and 24-54% for Fe). The outdoor concentrations of the other elements were not well predicted. The LUR modeled concentration only significantly correlated with measured personal Fe exposure in Utrecht and Ni and V in Helsinki. The LUR model predictions did not correlate with measured personal Cu exposure. After excluding observations with an indoor/outdoor ratio of >1.5, modeled Cu outdoor concentrations correlated with indoor concentrations in Helsinki and Utrecht and personal concentrations in Utrecht. The LUR model predictions were associated with measured outdoor, indoor and personal concentrations for all elements when the data for the three cities was pooled.

Conclusions Within-city modeled variation of elemental composition of $PM_{2.5}$ did not predict measured variation in personal exposure well.

Introduction

The association of air pollution and cardiovascular and respiratory health effects has been demonstrated in numerous epidemiological studies.[1,2] But there is less knowledge about which components are responsible for these health effects.[3-5] A few studies have evaluated short-term effects related to elemental composition of particles smaller than 2.5 µm ($PM_{2.5}$) and 10 µm (PM_{10}).[4] There are very few studies that have assessed effects related to long-term exposure to particle components.[6] One reason is the lack of spatially resolved long-term average particle component concentrations.

In epidemiological studies, land use regression (LUR) models for $PM_{2.5}$, PM_{10} and soot are often used to assess the spatial variability in exposure. These LUR models have the advantage that they have relatively simple input, less computation time and fine spatial resolution of predictions. Few LUR models have been developed for the elemental composition of $PM_{2.5}$ and PM_{10}. For the European Study of Cohorts for Air Pollution Effects (ESCAPE) standardized LUR models for eight elements were developed.[7] The eight elements of interest were copper (Cu), iron (Fe), potassium (K), nickel (Ni), sulfur (S), silicon (Si), vanadium (V) and zinc (Zn). These elements were selected from a range of elements because they were relatively well detected and represented different sources of particulate matter. Cu, Zn and Fe are transition elements associated with brake linings/ tire tread rubber emissions and Fe is furthermore associated with heavy diesel emissions and road dust.[8,9] Ni and V, also transition elements, are markers for fossil fuel combustion.[10,11] K is a marker for biomass burning and is also associated with road dust.[12,13] Si is a component of soil and S largely reflects long-range transport and secondary particle formation.[10] The authors of the ESCAPE elemental LUR models noted that elements for which non-traffic sources are important were modeled with lower predictive ability.[7]

Land use regression models predict the spatial variation of annual average ambient concentrations at the residential addresses of cohort participants in epidemiological studies. The ambient contrast may not transfer to contrasts in the personal exposure of the residents of the homes, due to less than 100% infiltration and time spent elsewhere than at home. On the other hand, measurement of personal exposure on a large enough scale for epidemiologic studies is unfeasible. However, the association between ambient concentrations and personal exposure can be investigated in smaller groups of subjects. In the **V**alidation of **E**SCAPE **E**xposure **E**stimate**S** using **P**ersonal exposure **A**ssessment (VE^{3}SPA) project, we evaluated the association of the modeled concentrations of Cu, Fe, K, Ni, S, Si, V and Zn with measured personal exposure in three ESCAPE study areas, Helsinki (Finland), Utrecht (the Netherlands) and Barcelona

(Spain). We previously reported on the association of LUR models for $PM_{2.5}$, NO_2 and soot with measured outdoor, indoor and personal exposure of this study.[14]

Materials & Methods

Land Use Regression Models

The LUR models for PM composition evaluated in this paper were developed within the ESCAPE project.[7] Briefly, models were based upon a standardized measurement campaign of $PM_{2.5}$, PM_{10}, NO_2 and soot in a large number of European study areas.[15] In each study area, PM was measured at 20 (in Helsinki/Turku and Barcelona) or 40 (in the Netherlands / Belgium area used for Utrecht) sites repeatedly. PM samples were analyzed for elemental composition using X-ray fluorescence (XRF). Potential predictor variables for the LUR model development covered traffic variables (traffic intensity, road length, distance to roads), land use, population density, altitude and local variables extracted for the study areas, using the geographical information system (GIS) ArcGIS 9.3 & 10 (ESRI, Redlands, CA, USA). The LUR models were developed for each study area separately using supervised stepwise selection.[7] The explained variability of the LUR models ranged from high (R^2 0.69-0.88 for Cu and Fe) to moderate (e.g. R^2 0.31-0.67 for S). The formulas for these models can be found in the online supplemental information (SI, Table S1).

Personal exposure study design

The design of the study has been described previously.[14] Briefly, in Helsinki (Finland), Utrecht (the Netherlands) and Barcelona (Spain) 15 non-smoking participants were recruited per city: 5 from suburban background, 5 from urban background and 5 from traffic sites, to get sufficient contrast in concentrations. The total study population thus consisted of 45 participants. Traffic sites were defined as streets with more than 10,000 vehicles per day. Background sites were defined as sites with less than 3,000 vehicles per day within 50 meters and with no other local sources nearby. Participants were selected from volunteers willing to follow specific prescribed time activity patterns. Volunteers were mostly students or retired. They were recruited by advertisements on campus and local newspapers. The total number of participants was limited to 15 subjects per city, because we attempted to characterize the average personal exposure per subject by a relatively large number of measurements per person (six 96-hour samples), requiring a one year field work period.

$PM_{2.5}$ personal exposure was monitored with BGI GK2.05SH cyclones at 3.5 l/min and BGI 400s personal exposure pumps (BGI inc., Waltham, Massachusetts) placed in backpacks that were carried by the participants. Simultaneously, outdoor and indoor samples were collected at the partic-

ipant homes using the same equipment. Outdoor units were placed at the façade on the street side of the homes at minimally 2 meters height, for example hanging from a window or on a balcony. Indoor units were placed in the living room at minimal 1 meter height. At every participant address six 96-hour measurements, spread over three different seasons, were conducted from Monday to Friday. Measurements were performed by three participants synchronously per city. To adjust for temporal variation, during every 96-hour measurement period concentrations were measured at a central reference site with the same equipment. The site was located at an urban or suburban background location in each city.

Measurements were performed from 01-03-2010 to 28-03-2011, for 30 96-hour sample periods in total for each city. In Utrecht and Barcelona this period was mainly after the ESCAPE study period; in Helsinki the study periods for VE^{3}SPA and ESCAPE overlapped substantially. The study area for model development was larger than the study area for personal monitoring: entire Netherlands versus Utrecht and surroundings; Helsinki and Turku area combined versus Helsinki. For Barcelona the study area was the same size.

During the measurements participants followed prescribed time activity patterns, a child activity pattern and an elderly activity pattern.[14] These patterns were designed to represent two groups thought to be sensitive to air pollution. During the first week of every sampling period, the participants followed the child pattern and during every second week the elderly pattern was followed. The difference between the two patterns was that during the child pattern less time was spent indoors at home, and more at "other indoor" locations. There were small differences between the prescribed patterns in the three cities to reflect differences in lifestyle between the countries. Table 1 shows that the participants were capable to follow the prescribed time activity patterns well.

Standard operating procedures were followed by the field technicians in each city (http://www.escapeproject.eu/vespa/manual.php). Furthermore, a field work instruction in Utrecht and site visits to Helsinki and Barcelona were organized to ensure the comparability of the results between cities.

Analysis of PM chemical composition

$PM_{2.5}$ mass was collected on Teflon filters (Zefon international, Ocala Florida) and was analyzed with energy dispersive x-ray fluorescence (ED-XRF) spectrometry to determine the elemental composition.[7] The samples were analyzed by Cooper Environmental Services (Portland, Oregon, USA), the same lab that analyzed the ESCAPE samples used to derive the evaluated LUR models. Samples were cooled during trans-

portation and were analyzed between October 2011 and February 2012. Quality assurance and control included NIST reference material analysis (SRM 1228 and SRM 987), repeated multi-elemental quality control standard analysis (Multi 30585) and for about 10% of the samples replicate analysis. All analyses fulfilled the QA-QC criteria.

Additionally, per city about 15 field blanks, 15 outdoor or indoor duplicates and 5 personal duplicates were taken. The mean field blank was determined per city and the detection limit (DL) per city was calculated as three times the standard deviation of the field blanks divided by the nominal sample volume of 20.2 m^3 (SI, table S2) The precision of measurements, expressed as the coefficient of variation (CV), was calculated with the field duplicates (SI, Table S3). The concentrations, in ng/m^3, were calculated as the analyzed sample concentration minus the mean blank concentration divided by the sampled volume and multiplied by the total filter area.

Table 1 The total number of hours that were spent on average by the volunteers at three microenvironments (at home, outdoors and other indoor locations) per 96 hours.

Child Pattern	Home			Outdoors			Other indoor		
	Goal[a]	Mean[b]	SD	Goal[a]	Mean[b]	SD	Goal[a]	Mean[b]	SD
Utrecht	64	63.9	3.7	8.0	8.0	2.1	24.0	23.9	2.7
Barcelona	52	57.4	9.5	12.0	8.6	2.1	32.0	29.9	8.6
Helsinki	68	66.6	5.4	8.0	3.5	1.1	20.0	24.1	4.0
Elderly Pattern	**Home**			**Outdoors**			**Other indoor**		
	Goal[a]	Mean[b]	SD	Goal[a]	Mean[b]	SD	Goal[a]	Mean[b]	SD
Utrecht	72	70.9	3.6	8.0	8.4	2.1	12.0	15.9	3.5
Barcelona	68	62.6	8.6	8.0	8.0	3.8	20.0	23.7	8.9
Helsinki	80	78.0	6.7	4.0	2.2	0.7	12.0	13.6	4.0

a Goal is the prescribed amount of time to be spent at the micro environment per 96 hours
b Mean is the actual mean number of hours that were spent at the microenvironment by the participants. SD is the standard deviation of the number of hours spend by the participants

Data analyses

The association of the LUR model predicted outdoor concentrations with the average measured outdoor, indoor and personal concentrations (corrected for temporal variation) was determined with linear regression per city. The coefficient of determination (Pearson's R^2) and the slope of the regression analyses are reported. Furthermore, the association of the modeled with measured outdoor/indoor/personal concentrations was determined in a pooled dataset, with and without an indicator variable for city to adjust for systematic differences between cities.

Because measurements were not performed simultaneously in all subjects, the measured outdoor/indoor/personal concentrations were adjusted for temporal variation using the continuous measurements at the reference site before calculating an average concentration per subject. For the temporal adjustment the same procedures were followed as in ESCAPE and VE^{3}SPA for $PM_{2.5}$ and $PM_{2.5}$ absorbance.[14,15] First, the difference between the overall mean concentration at the reference site and the weekly measurement at the reference site was calculated. Next, this concentration difference was added to the outdoor measurements in that sampling week. Personal and indoor concentrations were probably less affected by temporal variation than outdoor concentrations. The adjustment therefore involved the outdoor difference multiplied by the regression slopes of the linear relationship of the outdoor measurements with the indoor and personal measurements in each city. As slopes were below 1, the adjustment for the indoor and personal measurements was smaller than for the outdoor measurements. The used slopes can be found in supplemental information, Table S4. Finally, for the outdoor, indoor and personal measurements the average concentrations per participant were calculated, providing estimates for the annual average concentrations.

In Utrecht and Barcelona, for 2 of the 32 and 7 of the 30 sampling weeks missing data occurred at the reference site. These missing data were imputed using data from routine monitoring sites.[16] We only imputed if the squared correlation (R^2) with the available VE^{3}SPA measurements was higher than 0.5, as we preferred to retain some missing data rather than include poor predictions. In Utrecht, only for sulfur (S) the imputation formula met this criterion. In Barcelona, we could use an imputation formula for copper (Cu), nickel (Ni) and zinc (Zn) (SI, Table S4).

Participants were only included in the analyses if they had more than two measurements. In Barcelona, this resulted in the exclusion of 3 participants for the outdoor and personal analyses and five participants for the indoor analyses. In Barcelona, 12 participants were thus included for the outdoor and personal and 10 for the indoor analyses.

The indoor and personal concentrations are affected by particles infiltrated from outdoors and particles from indoor sources. For studies on outdoor air pollution, it has been argued that personal exposure to outdoor and indoor generated particles should be considered separately.[17] In an additional analysis, the indoor/outdoor ratios of individual samples were determined. We excluded observations with I/O ratios larger than 1.5 to assess the impact of indoor sources on the correlation between LUR modeled concentrations and measured indoor and personal exposure. We selected 1.5 as cut point to identify indoor observations clearly affected by indoor sources beyond measurement uncertainty.

Figure 1 Regression plots of the modeled concentrations versus measured concentrations for Fe and Zn (ng/m³).

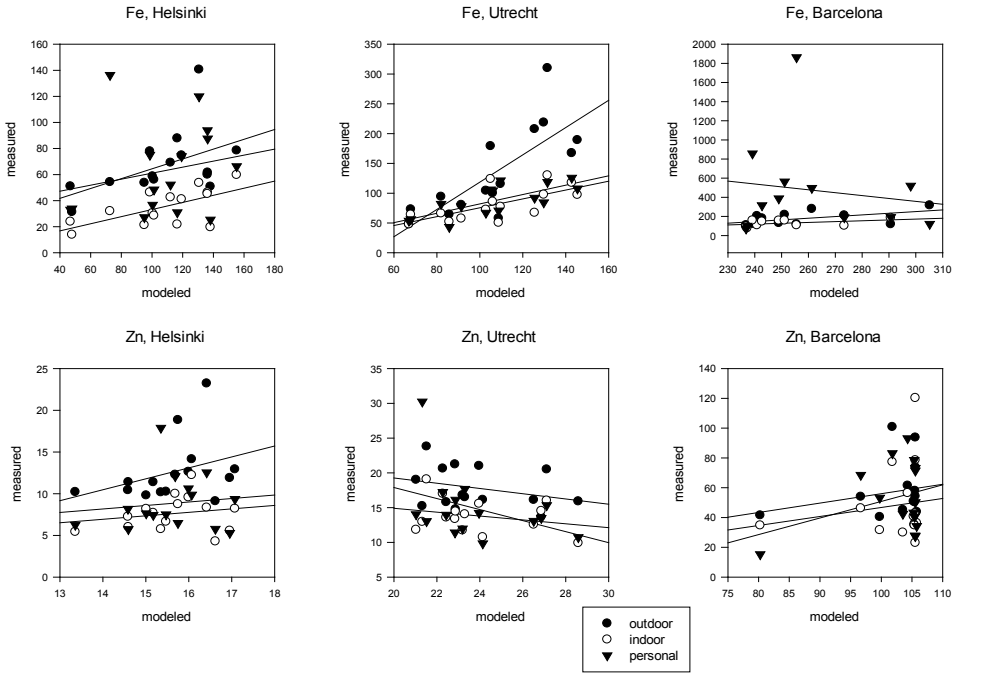
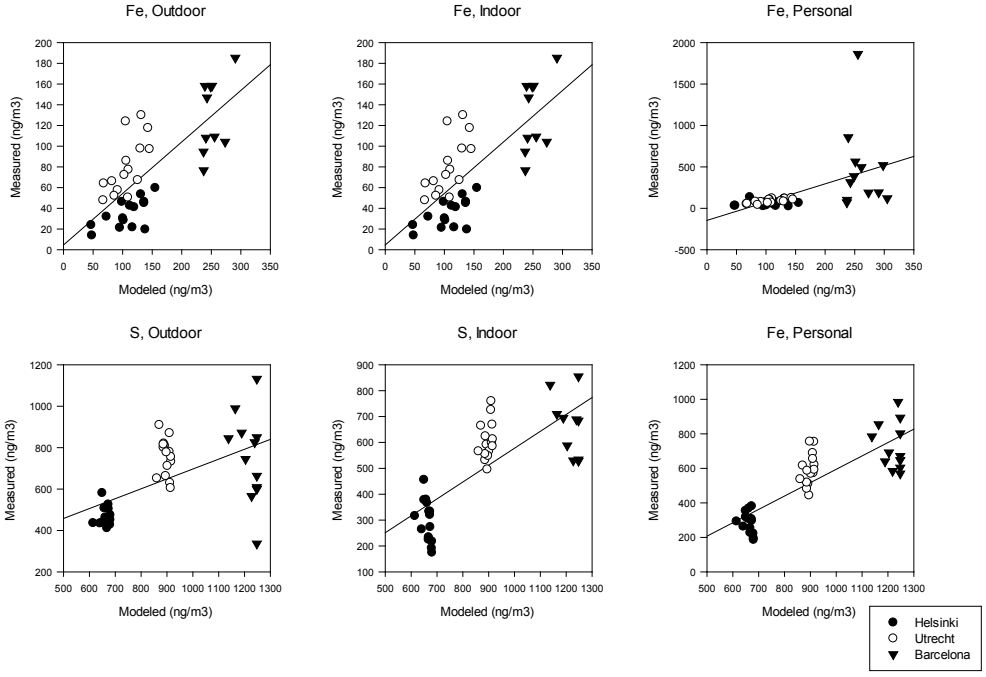


Figure 2 Regression plots of the pooled modeled concentrations versus measured concentrations for Fe and S (ng/m³).



Results

Distribution of concentrations

The mean, minimum and maximum averages of the modeled outdoor and measured outdoor, indoor and personal concentrations per city are shown in Table 2. For most elements, modeled concentrations were higher than the measured outdoor concentrations, especially in Barcelona. The range in modeled concentrations was small for several elements including S, Ni and V. For the traffic-related elements Cu and Fe the range of modeled concentrations was larger.

The median indoor/outdoor and personal/outdoor ratio for Cu and Si were higher than 1 in most cities (SI, Table S5). The Cu, K and Si personal concentrations were higher than the outdoor concentrations in all cities. Measured outdoor concentrations were significantly higher at traffic homes for Cu, Fe and Si (Table S6). Indoor and personal concentrations were increased for traffic homes, but statistically significantly for indoor Cu only.

Modeled versus measured concentrations

The modeled concentrations of Cu and Fe were (borderline, $p<0.10$) significantly correlated to the measured *outdoor* concentrations in all three cities (Table 3, Figure 1 and SI Figure S1-S3). In Utrecht and Barcelona, no correlation was found for the other elements. In Helsinki, modeled concentrations predicted also outdoor K, Si and V concentrations.

The *indoor* Fe concentrations were also correlated to the modeled outdoor concentrations in Helsinki and Utrecht, whereas no correlation was found for indoor Cu in any of the three cities. No associations were found for the other elements in Utrecht and Barcelona. Indoor V, S and Si (borderline significant) were associated with the modeled outdoor concentrations in Helsinki.

The modeled outdoor Fe concentrations were correlated to measured *personal* exposure in Utrecht, but not in Barcelona and Helsinki. In Helsinki the personal concentrations of Ni and V correlated with the modeled outdoor concentrations. No other significant correlations were found for the personal concentrations.

After excluding observations with indoor/outdoor concentration ratios above 1.5, modeled outdoor Fe and Cu were significantly correlated with measured average indoor concentrations in Helsinki and Utrecht (Table 4). A significant correlation between LUR modeled and measured personal Cu concentrations was found in Utrecht.

Table 2 The mean, minimum and maximum concentrations of the LUR modeled and corrected average measured outdoor, indoor and personal concentrations per city. $PM_{2.5}$ is in µg/m³, soot is in 10^{-5} m^{-1} and Cu, Zn, Fe, K, Ni, V, Si and S are in ng/m³.

	Helsinki											
	Modeled outdoor			Measured outdoor			Measured indoor			Measured personal		
Components	Mean	(Min-	Max)	Mean	(Min-	Max)	Mean	(Min-	Max)	Mean	(Min-	Max)
$PM_{2.5}$	8.5	(7.7-	9.5)	7.0	(5.4-	8.9)	7.6	(3.2-	22.5)	6.4	(2.9-	11.4)
Soot	1.1	(1.0-	1.4)	0.9	(0.6-	1.4)	0.8	(0.4-	1.7)	0.8	(0.4-	1.5)
Cu	2.1	(0.6-	3.6)	2.3	(1.3-	5.8)	6.2	(1.4-	17.5)	6.1	(1.8-	13.9)
Zn	15.6	(13.4-	17.1)	12.5	(9.1-	23.2)	7.6	(4.3-	12.2)	8.8	(5.3-	17.9)
Fe	107.1	(46.8-	155.2)	67.2	(31.3-	140.7)	35.1	(13.9-	59.8)	62.7	(25.3-	136.3)
K	115.2	(105.6-	123.4)	74.8	(61.6-	130.9)	86.6	(38.6-	350.1)	78.8	(40.9-	145.8)
Ni	1.6	(0.8-	2.0)	1.0	(0.1-	1.8)	0.6	(0.0-	1.4)	0.6	(0.1-	1.2)
V	3.2	(1.6-	4.4)	2.0	(1.0-	3.2)	1.2	(0.3-	2.3)	1.2	(0.1-	2.4)
Si	145.3	(89.6-	211.6)	84.8	(52.2-	137.2)	73.8	(20.5-	113.7)	91.3	(37.5-	164.2)
S	662.4	(614.3-	680.3)	466.7	(411.3-	581.0)	297.5	(174.5-	455.8)	284.9	(185.9-	380.5)
	Utrecht											
	Modeled outdoor			Measured outdoor			Measured indoor			Measured personal		
Components	Mean	(Min-	Max)	Mean	(Min-	Max)	Mean	(Min-	Max)	Mean	(Min-	Max)
$PM_{2.5}$	17.1	(14.5-	19.2)	15.3	(11.5-	19.7)	12.0	(7.2-	20.5)	11.2	(8.5-	14.7)
Soot	1.5	(1.1-	2.1)	1.3	(0.9-	2.4)	1.1	(0.7-	1.7)	1.0	(0.7-	1.3)
Cu	4.4	(2.7-	6.7)	5.3	(2.1-	13.2)	7.3	(3.0-	18.9)	6.0	(2.4-	11.5)
Zn	23.7	(21.0-	28.6)	17.6	(13.7-	23.8)	13.8	(9.9-	19.1)	14.8	(9.8-	30.2)
Fe	107.8	(66.9-	145.5)	130.8	(48.2-	310.1)	80.6	(47.8-	130.0)	87.4	(43.1-	125.7)
K	114.2	(110.8-	123.5)	73.3	(51.7-	90.7)	117.9	(45.1-	326.4)	93.8	(58.7-	240.7)
Ni	2.0	(1.9-	2.1)	0.8	(0.6-	1.1)	0.6	(0.3-	0.9)	0.7	(0.3-	1.1)

Table 2 continued

V	3.2	(2.9-	3.4)	1.8	(1.4-	2.2)	1.3	(0.9-	2.0)	1.3	(0.9-	1.7)
Si	93.2	(82.0-	119.8)	59.4	(-33.9*-	96.1)	72.2	(23.5-	136.5)	83.6	(41.1-	132.0)
S	894.6	(858.4-	915.5)	745.8	(602.1-	909.3)	606.3	(496.0-	759.7)	593.3	(443.5-	755.1)
						Barcelona						
	Modeled outdoor			**Measured outdoor**			**Measured indoor**			**Measured personal**		
Components	**Mean**	**(Min-**	**Max)**	**Mean**	**(Min-**	**Max)**	**Mean**	**(Min-**	**Max)**	**Mean**	**(Min-**	**Max)**
$PM_{2.5}$	18.1	(13.6-	25.1)	17.5	(12.6-	23.1)	16.5	(11.4-	28.0)	21.7	(13.4-	47.0)
Soot	2.9	(1.7-	4.0)	2.6	(1.7-	3.7)	2.1	(1.4-	3.1)	2.2	(1.6-	2.8)
Cu	19.3	(11.8-	25.1)	9.9	(5.4-	19.0)	10.3	(4.6-	21.6)	13.8	(4.1-	34.7)
Zn	102.4	(80.3-	105.8)	56.6	(36.6-	100.8)	48.2	(23.0-	120.3)	53.5	(15.3-	93.1)
Fe	261.2	(235.7-	305.2)	175.6	(96.8-	317.0)	129.9	(76.6-	185.3)	473.2	(72.0-	1863.0)
K	163.6	(104.0-	208.2)	141.5	(67.4-	208.5)	125.4	(61.7-	198.2)	212.5	(117.3-	467.9)
Ni	3.7	(1.7-	5.0)	2.9	(0.3-	9.6)	2.3	(1.0-	7.1)	2.6	(1.4-	5.1)
V	16.0	(12.6-	17.2)	5.1	(1.5-	8.3)	4.3	(2.5-	6.4)	4.9	(3.3-	7.5)
Si	290.5	(229.6-	331.0)	107.4	(55.8-	154.2)	138.8	(81.8-	233.5)	425.6	(91.7-	1184.6)
S	1225.3	(1138.1-	1247.4)	757.1	(336.0-	1131.7)	663.4	(528.4-	854.7)	727.0	(569.6-	984.2)

Measurements for model development and personal exposure in same year in Helsinki and subsequent years in Barcelona and Utrecht
* This value, negative because of the reference site correction, was from volunteer N09 and did not influence the results of the analyses

Table 3 Association between LUR modeled and measured average outdoor, indoor and personal concentrations per city for $PM_{2.5}$, Soot and the components Cu, Fe, K, Ni, S, Si, V, Zn.

Outdoor	Helsinki				Utrecht				Barcelona			
Components	R^2	β	p	N	R^2	β	p	N	R^2	β	p	N
$PM_{2.5}$	0.21	0.72	0.08'	15	0.43	1.09	0.01*	15	0.10	0.37	0.25	15
Soot	0.57	1.02	0.00*	15	0.75	1.18	0.00*	15	0.33	0.65	0.02*	15
Cu	0.35	0.68	0.02*	15	0.67	1.97	0.00*	15	0.34	0.50	0.02*	15
Fe	0.24	0.38	0.06'	15	0.58	2.29	0.00*	15	0.29	1.74	0.07'	12
K	0.34	1.71	0.02*	15	0.00	0.04	0.96	15	0.05	0.32	0.49	12
Ni	0.16	0.55	0.13	15	0.04	-0.35	0.47	15	0.01	-0.18	0.79	15
S	0.00	0.12	0.87	15	0.07	-1.40	0.35	15	0.14	-2.08	0.23	12
Si	0.35	0.33	0.02*	15	0.11	0.81	0.23	15	0.00	-0.02	0.94	12
V	0.35	0.38	0.02*	15	0.00	0.02	0.96	15	0.10	-0.37	0.31	12
Zn	0.11	1.29	0.22	15	0.09	-0.38	0.28	15	0.05	0.63	0.42	15
Indoor	**Helsinki**				**Utrecht**				**Barcelona**			
Components	R^2	β	p	N	R^2	β	p	N	R^2	β	P	N
$PM_{2.5}$	0.06	2.10	0.38	15	0.01	0.26	0.72	15	0.00	0.00	0.99	15
Soot	0.30	1.84	0.03*	15	0.64	0.69	0.00*	15	0.36	0.53	0.02*	15
Cu	0.04	0.93	0.45	15	0.11	1.08	0.23	15	0.09	0.27	0.28	15
Fe	0.40	0.27	0.01*	15	0.47	0.74	0.01*	15	0.19	0.88	0.21	10
K	0.01	1.23	0.75	15	0.00	-0.54	0.93	15	0.00	0.02	0.97	10
Ni	0.17	0.50	0.13	15	0.01	0.15	0.77	15	0.00	0.01	0.99	15
S	0.21	-2.05	0.09'	15	0.10	1.35	0.26	15	0.17	-1.21	0.24	10
Si	0.25	0.37	0.06'	15	0.01	-0.19	0.77	15	0.02	-0.19	0.70	10
V	0.37	0.40	0.02*	15	0.02	0.32	0.59	15	0.05	-0.15	0.54	10
Zn	0.04	0.40	0.49	15	0.07	-0.28	0.33	15	0.02	0.61	0.58	15
Personal	**Helsinki**				**Utrecht**				**Barcelona**			
Components	R^2	β	p	N	R^2	β	p	N	R^2	β	p	N
$PM_{2.5}$	0.08	1.08	0.32	15	0.06	-0.37	0.36	15	0.00	-0.15	0.86	15
Soot	0.39	1.41	0.01*	15	0.44	0.40	0.01*	15	0.20	0.29	0.09'	15
Cu	0.03	0.61	0.52	15	0.13	0.66	0.20	15	0.04	-0.34	0.47	15
Fe	0.05	0.23	0.45	15	0.56	0.78	0.00*	15	0.02	-3.03	0.64	12
K	0.09	1.68	0.27	15	0.00	0.02	1.00	15	0.03	-0.65	0.59	12
Ni	0.30	0.56	0.04*	15	0.00	0.11	0.86	15	0.04	-0.25	0.48	15
S	0.10	-1.08	0.24	15	0.18	2.34	0.11	15	0.02	-0.51	0.65	12
Si	0.11	0.29	0.23	15	0.00	-0.03	0.96	15	0.15	3.73	0.21	12
V	0.47	0.43	0.01*	15	0.06	0.47	0.37	15	0.12	-0.23	0.28	12
Zn	0.01	0.38	0.69	15	0.15	-0.79	0.16	15	0.10	1.11	0.25	15

The coefficient of determination (R^2), the p value (p) and the number of included sites (N) of the regression analysis of the modeled concentrations versus measured concentrations for $PM_{2.5}$, soot, and the elements Cu, Fe, K, Ni, S, Si, V and Zn. Concentrations adjusted using the absolute differences method. N less than 15 in Barcelona because of missing elemental data at the reference site resulting in fewer than 3 valid measurements. Cu, Ni and Zn could be reliably imputed.

* significant at the p<0.05 level ' significant at the p<0.10 level

Pooled analyses

In contrast to the within-city analyses, the outdoor, indoor and personal concentrations for all elements were significantly correlated to the modeled concentrations in the pooled dataset (Table 5, Figure 2 and SI Figure S4-S6). Only the indoor potassium (K) concentrations did not correlate with the modeled concentrations. When an indicator for city was added to the model, the modeled concentration was much less consistently correlated with measured concentrations, indicating systematic concen-

Table 4 Association between LUR modeled and measured average indoor and personal concentrations per city for $PM_{2.5}$, Soot and the components Cu, Fe, K, Ni, S, Si, V, Zn after observations with an indoor/outdoor Ratio>1.5 were excluded (only including participants with >2 observations)

Indoor	Helsinki			Utrecht			Barcelona		
Components	R^2	p	N	R^2	p	N	R^2	P	N
$PM_{2.5}$	0.16	0.14	15	0.03	0.55	15	0.02	0.63	15
Soot	0.37	0.02*	15	0.64	0.00*	15	0.38	0.02*	15
Cu	0.70	0.00*	9	0.35	0.03	14	0.08	0.29	15
Fe	0.41	0.01*	15	0.45	0.01	15	0.02	0.72	10
K	0.06	0.39	15	0.07	0.42	12	0.01	0.84	10
Ni	0.16	0.14	15	0.00	0.86	15	0.00	0.85	15
S	0.21	0.09’	15	0.11	0.22	15	0.21	0.18	10
Si	0.48	0.00*	15	0.01	0.70	13	0.12	0.44	7
V	0.37	0.02*	15	0.02	0.58	15	0.08	0.44	10
Zn	0.04	0.49	15	0.19	0.11	15	0.03	0.57	15
Personal	**Helsinki**			**Utrecht**			**Barcelona**		
Components	R^2	p	N	R^2	p	N	R^2	P	N
$PM_{2.5}$	0.13	0.18	15	0.05	0.41	15	0.00	0.94	15
Soot	0.37	0.02*	15	0.42	0.01*	15	0.18	0.12	15
Cu	0.41	0.07’	9	0.32	0.03*	14	0.04	0.50	14
Fe	0.12	0.21	15	0.52	0.00*	15	0.03	0.57	12
K	0.11	0.22	15	0.01	0.70	13	0.04	0.55	12
Ni	0.25	0.06’	15	0.00	0.91	15	0.01	0.66	15
S	0.10	0.24	15	0.19	0.11	15	0.02	0.66	12
Si	0.32	0.04*	14	0.00	0.83	13	0.16	0.28	9
V	0.47	0.01*	15	0.05	0.41	15	0.19	0.16	12
Zn	0.01	0.69	15	0.14	0.17	15	0.10	0.25	15

The coefficient of determination (R^2), the p value (p) and the number of included measurements (N)

* significant at the p<0.05 level ` significant at the p<0.10 level

tration differences between cities. Borderline significant associations were found between LUR modeled and measured personal concentrations for Fe and V.

Additional analyses

The association of the measured outdoor with the measured indoor and personal concentrations are shown in Table 6. In all countries measured indoor and personal concentrations were better correlated with measured outdoor concentrations than with the modeled outdoor concentrations. The indoor Ni concentrations were significantly correlated with the outdoor concentrations in all three cities. Zn indoor concentrations had a significant association with measured outdoor concentrations in Utrecht and Barcelona and borderline in Helsinki. Indoor Fe concentrations were correlated in Utrecht and Helsinki and S and V in Barcelona and Helsinki respectively. Si indoor concentrations were borderline significantly correlated with Si in outdoor air in Helsinki.

Personal Ni, S and V concentrations were significantly correlated with the measured outdoor concentrations in Helsinki (Table 6). Personal Fe was significantly correlated with measured outdoor in Utrecht and borderline in Helsinki. Personal Si concentrations were significantly correlated with measured outdoor in Utrecht and personal Zn in Barcelona.

The personal concentrations were better associated with the indoor concentrations than with the outdoor concentrations (Table 6). Except for Zn, personal concentrations of all elements were statistically significantly correlated with the indoor concentrations in Helsinki and Utrecht.

Discussion

Previously developed LUR models for elemental composition of $PM_{2.5}$ predicted the within-city variation of outdoor Cu and Fe (as measured in this study) moderately well. The outdoor concentrations of the other elements were not well predicted. Significant correlations between the LUR models and measured personal exposures were observed only for Fe in Utrecht and Ni and V in Helsinki. The LUR model results did not correlate with measured personal Cu exposure. Measured outdoor elemental concentrations correlated better with measured indoor and personal exposure. For most elements, the LUR model predictions were associated with measured outdoor, indoor and personal concentrations when the data for the three cities was pooled.

Table 5 Association between LUR modeled and measured average outdoor, indoor and personal concentrations in the pooled dataset for the components $PM_{2.5}$, Soot, Cu, Fe, K, Ni, S, Si, V, Zn

Outdoor	without city indicators			with city indicators			
Components	R^2	β	p	R^2	βmod	pmod	N
$PM_{2.5}$	0.81	0.97	0.00*	0.84	0.50	0.01*	45
Soot	0.85	0.88	0.00*	0.85	0.80	0.00*	45
Cu	0.65	0.43	0.00*	0.71	0.62	0.00*	45
Fe	0.35	0.60	0.00*	0.55	1.22	0.00*	42
K	0.44	0.90	0.00*	0.54	0.36	0.14	42
Ni	0.23	0.70	0.00*	0.37	-0.10	0.77	45
S	0.33	0.48	0.00*	0.60	-1.56	0.05*	42
Si	0.26	0.21	0.00*	0.29	0.22	0.16	42
V	0.56	0.00	0.00*	0.63	-0.19	0.25	42
Zn	0.79	0.00	0.00*	0.79	0.53	0.20	45
Indoor	**without city indicators**			**with city indicators**			
Components	**R^2**	**β**	**P**	**R^2**	**βmod**	**Pmod**	**N**
$PM_{2.5}$	0.35	0.68	0.00*	0.46	0.12	0.74	45
Soot	0.79	0.72	0.00*	0.79	0.63	0.00*	45
Cu	0.20	0.24	0.00*	0.21	0.36	0.13	45
Fe	0.57	0.50	0.00*	0.77	0.50	0.00*	40
K	0.01	0.35	0.47	0.06	0.07	0.93	40
Ni	0.34	0.66	0.00*	0.46	0.06	0.81	45
S	0.59	0.65	0.00*	0.80	-0.94	0.11	40
Si	0.35	0.32	0.00*	0.40	0.13	0.50	40
V	0.74	0.00	0.00*	0.77	-0.01	0.95	40
Zn	0.62	0.00	0.00*	0.63	0.51	0.37	45
Personal	**without city indicators**			**with city indicators**			
Components	**R^2**	**β**	**P**	**R^2**	**βmod**	**Pmod**	**N**
$PM_{2.5}$	0.35	1.01	0.00*	0.63	-0.15	0.74	45
Soot	0.83	0.70	0.00*	0.86	0.37	0.00*	45
Cu	0.29	0.40	0.00*	0.38	-0.22	0.42	45
Fe	0.28	2.21	0.00*	0.33	-0.33	0.83	42
K	0.18	1.36	0.01*	0.40	-0.56	0.40	42
Ni	0.43	0.71	0.00*	0.68	-0.15	0.42	45
S	0.70	0.77	0.00*	0.80	-0.16	0.80	42
Si	0.42	1.84	0.00*	0.45	1.62	0.10'	42
V	0.80	0.00	0.00*	0.85	-0.07	0.50	42
Zn	0.71	0.00	0.00*	0.72	0.90	0.08	45

The R-square (R^2), slope (β), p-value (p), slope for the model (βmod), p-value for the model (pmod), the number of observations used (N).
*significant at the p<0.05 level 'significant at the p<0.10 level

Table 6 Regression of the average measured outdoor versus the measured indoor/personal elemental concentrations.

Components	Outdoor versus Indoor											
	Helsinki				Utrecht				Barcelona			
	R^2	β	p	N	R^2	β	p	N	R^2	β	p	N
$PM_{2.5}$	0.29	2.99	0.04*	15	0.01	0.18	0.67	15	0.00	0.04	0.90	15
Soot	0.27	1.27	0.05*	15	0.86	0.59	0.00*	15	0.76	0.68	0.00*	15
Cu	0.07	1.04	0.33	15	0.35	0.80	0.02*	15	0.31	0.59	0.03*	15
Fe	0.38	0.34	0.01*	15	0.67	0.30	0.00*	15	0.01	0.08	0.76	10
K	0.00	0.20	0.88	15	0.10	2.66	0.24	15	0.59	0.64	0.01*	10
Ni	0.61	0.71	0.00*	15	0.65	0.84	0.00*	15	0.91	0.67	0.00*	15
S	0.36	1.07	0.02*	15	0.11	0.27	0.23	15	0.80	0.59	0.00*	10
Si	0.19	0.59	0.10’	15	0.36	0.55	0.02*	15	0.02	-0.22	0.69	10
V	0.66	0.83	0.00*	15	0.17	0.54	0.12	15	0.86	0.66	0.00*	10
Zn	0.19	0.23	0.11	15	0.38	0.51	0.01*	15	0.80	1.22	0.00*	15
Components	**Outdoor versus Personal**											
	Helsinki				Utrecht				Barcelona			
	R^2	β	p	N	R^2	β	p	N	R^2	β	p	N
$PM_{2.5}$	0.32	1.43	0.03*	15	0.09	-0.26	0.28	15	0.10	-0.82	0.25	15
Soot	0.29	0.89	0.04*	15	0.53	0.32	0.00*	15	0.04	0.12	0.46	15
Cu	0.05	0.63	0.44	15	0.24	0.38	0.06’	15	0.03	-0.36	0.51	15
Fe	0.20	0.64	0.09’	15	0.44	0.23	0.01*	15	0.04	-1.41	0.55	11
K	0.04	0.39	0.46	15	0.04	0.90	0.49	15	0.02	0.40	0.67	11
Ni	0.75	0.66	0.00*	15	0.13	0.49	0.18	15	0.22	0.25	0.08’	15
S	0.28	0.70	0.04*	15	0.00	0.00	0.99	15	0.16	0.25	0.23	11
Si	0.09	0.49	0.27	15	0.34	0.51	0.02*	15	0.20	-4.38	0.17	11
V	0.78	0.87	0.00*	15	0.10	0.37	0.25	15	0.08	0.15	0.41	11
Zn	0.04	0.17	0.49	15	0.03	-0.28	0.53	15	0.45	0.83	0.01*	15

Table 6 continued

Components	Indoor versus Personal											
	Helsinki				Utrecht				Barcelona			
	R^2	β	p	N	R^2	β	p	N	R^2	β	p	N
$PM_{2.5}$	0.61	0.35	0.00*	15	0.15	0.22	0.16	15	0.02	-0.32	0.60	15
Soot	0.85	0.62	0.00*	15	0.79	0.62	0.00*	15	0.11	0.24	0.24	15
Cu	0.74	0.65	0.00*	15	0.76	0.49	0.00*	15	0.03	0.33	0.52	15
Fe	0.41	1.62	0.01*	15	0.62	0.76	0.00*	15	0.00	0.41	0.95	9
K	0.64	0.32	0.00*	15	0.75	0.50	0.00*	15	0.06	0.78	0.53	9
Ni	0.69	0.70	0.00*	15	0.22	0.60	0.07’	15	0.18	0.32	0.11	15
S	0.76	0.65	0.00*	15	0.37	0.77	0.02*	15	0.33	0.68	0.11	9
Si	0.61	0.93	0.00*	15	0.35	0.57	0.02*	15	0.06	1.89	0.54	9
V	0.77	0.85	0.00*	15	0.48	0.62	0.00*	15	0.07	0.27	0.50	9
Zn	0.08	0.47	0.31	15	0.03	0.34	0.54	15	0.32	0.52	0.03	15

The R-square (R^2), slope (β) and p-value (p).
* significant at the $p<0.05$ level, ‘ significant at the $p<0.10$ level

Non-tailpipe emissions: Cu, Fe and Zn

The ESCAPE LUR models predicted the intra-urban variation of outdoor Cu and Fe but not Zn concentrations moderately well across the three cities. Cu, Fe and Zn are components in non-tailpipe emissions from road traffic, related to brake, tire and road wear. LUR models, including traffic predictor variables, for Cu and Fe had high percentage explained variability (R^2), ranging from 0.69 to 0.88 (SI Table S1).[7]

The lower R^2 found in our study using completely independent data is consistent with recent studies showing that model R^2 are inflated when based on a small training dataset used to develop the model.[18-20] Consistent with these studies, the drop in R^2 was smaller for Utrecht, where the model was based upon 40 sites compared to Helsinki and Barcelona where the model was based upon 20 sites. Another difference in Helsinki was that on average the sampling monitors for the VE^{3}SPA study were placed higher than in the other two cities, especially at the street sites (15 m versus 3-5 m in Utrecht and Barcelona). This may have reduced the contrast in air pollution related to differences in traffic intensity. In contrast, all ESCAPE samples were taken on the ground or first floor.[21]

The lack of correlation for Zn could be due to a poor LUR model in Helsinki (model R^2 0.21) and possibly the lack of small-scale traffic variables (e.g. 25 to 100 m buffers) in the Zn LUR models (SI Table S1).

Only for Fe we also found some evidence (Utrecht, Helsinki) that indoor and/or personal exposure was correlated with modeled outdoor concentrations. Previously we also did not find measured personal and indoor $PM_{2.5}$, to be associated with modeled outdoor concentrations.[14] Indoor sources probably contributed to the low correlations of LUR modeled with indoor and personal Zn, Cu and Fe concentrations. The high indoor/outdoor ratios for Cu, suggests that Cu was especially influenced by indoor sources (SI Table S5) in some of the homes. In the study by Molnar et al., suggested Cu sources were cooking and frying and electrical appliances like vacuum cleaners and hair dryers.[22] Also indoor sources for K and Cu were reported in a source apportionment study of indoor $PM_{2.5}$ in Amsterdam and Helsinki.[23] After excluding observations clearly affected by indoor sources, as indicated by indoor/outdoor ratios>1.5, correlations between modeled Cu and indoor and/or personal exposure improved in Utrecht and Helsinki. Based on this, it is plausible that the modeled outdoor Fe and Cu concentrations do correlate with indoor/personal elemental concentrations from outdoor origin. This is the relevant correlation for studies evaluating the health effects of outdoor generated air pollutants[24], e.g. studies of the health effects of non-tailpipe emissions of road traffic. For studies that aim to evaluate the health effects of specific components (Cu, Fe) irrespective of their source, the (low) correlations including all observations is relevant. A further explanation for the low correlation with indoor and

personal exposures is limited infiltration indoors, as Cu and Fe are found in the coarse tail (~1-2.5 μm) of the fine particle fraction distribution.[25] Coarse particles penetrate indoors less efficiently than fine particles.[26]

K, Ni, S, Si, V models

For these elements, the LUR models did explain the outdoor measurements in Helsinki but not in Utrecht and Barcelona. Explanations for the absence of correlations for these elements in the latter two cities probably include a combination of the following factors: 1. Relatively poor LUR models; 2. The study area of VE^{3}SPA is smaller than in ESCAPE; 3. Low precision of the VE^{3}SPA measurements; 4. Missing data at the reference site.

Consistent with the *first* explanation is that the model and cross-validation R^2 values for most of the elemental ESCAPE models were lower than for the main components ($PM_{2.5}$ and soot) and for the non-tailpipe elements Cu/Fe.[7] For eight of the 15 models for the elements K, Ni, S, Si, V the model R^2 was below 0.50 (SI Table S1). These elements are related to sources that are more difficult to characterize with land use variables available in GIS than traffic, e.g. wood smoke for K and specific industrial sources or residual oil burning for V and Ni.[7]

In Utrecht, the *second* explanation is important for especially the components Ni and V, as the ESCAPE study area (entire Netherlands) is much larger than the VE^{3}SPA study area (Utrecht and surroundings). The ESCAPE models for Ni and V included presence of a port and the X-coordinate. The X-coordinate represents distance to residual oil burning from ships and the Rotterdam harbor and industrial area (SI Table S1). On a national scale these models explained a large fraction of variability with plausible predictors. These models, however, do not predict much variability in a small area such as the Utrecht metropolitan area. This finding suggests that national models may not perform well in smaller areas, depending on the distribution of source terms available in GIS. For Cu and Fe this was less of an issue as traffic sources are present everywhere. The Utrecht area is not well-suited to test the modeled-measured agreement for Ni and V on a national scale. In contrast, the Ni and V LUR models performed better in Helsinki, because they did not include the variable of presence of a port.

Relatively poor precision of measurements (SI Table S3) is an unlikely explanation as the average concentration based on 6 samples is still well characterized. A CV of 30% for individual samples results in an uncertainty of about 12% of the mean. A further argument against this explanation is that we did observe high temporal correlations between measured elemental exposures.[16] Temporal correlations are based upon individual

samples and are hence more sensitive to low precision.

The fourth explanation, missing data at the reference site, may have contributed in Barcelona, which had the most missing data. This is not an issue in Helsinki and unlikely in Utrecht. As elements are not measured routinely, we had fewer possibilities to impute missing values at the reference site than we had for the main components.

Indoor sources likely have contributed to the lack of association with the measured indoor and personal concentrations, as shown in our analysis of observations remaining after excluding samples with indoor/outdoor ratios of >1.5.

Pooled analysis

We found that LUR modeled outdoor concentrations were well correlated with measured outdoor, indoor and personal concentrations when the data for the three cities were pooled. This observation is important for studies that make use of between-city contrasts of exposure. The largest fractions of the R^2s can be explained by the concentration contrasts between the three cities. When we included city indicators, only personal Si and Zn showed borderline significant associations with the modeled outdoor concentrations. For S this is consistent with the fact that long-range transport is the most important source of S concentrations, with only modest intra-urban variations.

In conclusion, the best LUR models for ambient concentrations were found for Fe and Cu, components for which local traffic is an important source. However, within-city modeled variation did not effectively predict variation in personal exposure to the elements we studied; Cu, Zn, Fe, K, Ni, V, Si or S. Correlations with indoor and/or personal Cu improved after limiting the influence of indoor sources.

Limitations

A limitation of this study is the small sample size, which made it difficult to find significant effects in within-city analyses (R^2 needed to be >0.25 to be significant at the $p<0.05$ level). For this study the focus was to estimate the yearly average for the participants, so we had long (96-hour) sampling periods and six measurements per participant. This resulted in a study period of one year and a limited number of participants. The sample was meant to represent specific time-activity patterns and not a city population.
It remains challenging to obtain sufficient personal monitoring data for evaluation of long-term exposure estimates.[14]

References

1. Pope III, C.A. and Dockery, D.W. Health effects of fine particulate air pollution: Lines that connect. *EM: Air and Waste Management Association's Magazine for Environmental Managers* **2006,** *54,* 709-742.

2. Brunekreef, B. and Holgate, S.T. Air pollution and health. *Lancet* **2002,** *360,* 1233-1242.

3. Kelly, F.J. and Fussell, J.C. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmos. Environ.* **2012,** *60,* 504-526.

4. Stanek, L.W.; Sacks, J.D.; Dutton, S.J.; Dubois, J.J.B. Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results. *Atmos. Environ.* **2011,** *45,* 5655-5663.

5. WHO Review of evidence on health aspects of air pollution – REVIHAAP Project. **2013.** http://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/2013/review-of-evidence-on-health-aspects-of-air-pollution-revihaapproject-final-technical-report [accessed October 15 2013]

6. Ostro, B.; Lipsett, M.; Reynolds, P., et al Long-term exposure to constituents of fine particulate air pollution and mortality: Results from the California Teachers Study. *Environ. Health Perspect.* **2010,** *118,* 363-369.

7. De Hoogh, K.; Wang, M.; Adam, M., et al Development of land use regression models for particle composition in twenty study areas in Europe. *Environ. Sci. Technol.* **2013,** *47,* 5778-5786.

8. Hjortenkrans, D.S.; Bergback, B.G.; Haggerud, A.V. Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. *Environ. Sci. Technol.* **2007,** *41,* 5224-5230.

9. Amato, F.; Pandolfi, M.; Escrig, A., et al Quantifying road dust resuspension in urban environment by Multilinear Engine: A comparison with PMF2. *Atmos. Environ.* **2009,** *43,* 2770-2780.

10. Viana, M.; Kuhlbusch, T.A.J.; Querol, X., et al Source apportionment of particulate matter in Europe: A review of methods and results. *J. Aerosol Sci.* **2008,** *39,* 827-849.

11. Johansson, C.; Norman, M.; Burman, L. Road traffic emission factors for heavy metals. *Atmos. Environ.* **2009,** *43,* 4681-4688.

12. Gietl, J.K.; Lawrence, R.; Thorpe, A.J.; Harrison, R.M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* **2010,** *44,* 141-146.

13. Pio, C.A.; Legrand, M.; Alves, C.A., et al Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. *Atmos. Environ.* **2008,** *42,* 7530-7543.

14. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Agreement of land use regression models with personal exposure measurements of particulate matter and nitrogen oxides air pollution. *Environ. Sci. Technol.* **2013,** *47,* 8523-8531.

15. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression

models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. *Environ. Sci. Technol.* **2012,** *46,* 11195-11205.

16. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Temporal associations of ambient PM2.5 elemental concentrations with indoor and personal concentrations. *Atmos. Environ.* **2014,** *86,* 203-211.

17. Wilson, W.E. and Brauer, M. Estimation of ambient and non-ambient components of particulate matter exposure from a personal monitoring panel study. *J. Expos. Sci. Environ. Epidemiol.* **2006,** *16,* 264-274.

18. Basagaña, X.; Rivera, M.; Aguilera, I., et al Effect of the number of measurement sites on land use regression models in estimating local air pollution. *Atmos. Environ.* **2012,** *54,* 634-642.

19. Wang, M.; Beelen, R.; Eeftens, M.; Meliefste, K.; Hoek, G.; Brunekreef, B. Systematic evaluation of land use regression models for NO 2. *Environ. Sci. Technol.* **2012,** *46,* 4481-4489.

20. Wang, M.; Beelen, R.; Basagana, X., et al Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project. *Environ. Sci. Technol.* **2013,** *47,* 4357-4364.

21. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric Environment* **2012,** *62,* 303-317.

22. Molnar, P.; Bellander, T.; Sallsten, G.; Boman, J. Indoor and outdoor concentrations of PM2.5 trace elements at homes, preschools and schools in Stockholm, Sweden. *J. Environ. Monit.* **2007,** *9,* 348-357.

23. Yli-Tuomi, T.; Lanki, T.; Hoek, G.; Brunekreef, B.; Pekkanen, J. Determination of the sources of indoor PM2.5 in Amsterdam and Helsinki. *Environ. Sci. Technol.* **2008,** *42,* 4440-4446.

24. Sarnat, J.A.; Brown, K.W.; Schwartz, J.; Coull, B.A.; Koutrakis, P. Ambient gas concentrations and personal particulate matter exposures: Implications for studying the health effects of particles. *Epidemiology* **2005,** *16,* 385-395.

25. Birmili, W.; Allen, A.G.; Bary, F.; Harrison, R.M. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environ. Sci. Technol.* **2006,** *40,* 1144-1153.

26. Sarnat, S.E.; Coull, B.A.; Ruiz, P.A.; Koutrakis, P.; Suh, H.H. The influences of ambient particle composition and size on particle infiltration in Los Angeles, CA, residences. *J. Air Waste Manag. Assoc.* **2006,** *56,* 186-196.

Supplemental Information

LUR Models

Table S1 Land Use Regression (LUR) models for Cu, Fe, K, Ni, S, Si, V and Zn.[1]

Study area	LUR model [1]	R^2 of model	R^2 validation	RMSE (validation) (ng/m^3) [2]	Number of sites	Measured concentration (ng/m^3) [3]
Cu						
Finland, Helsinki	0.5 +7.3E-04*HHOLD_300L +1.5E-07*TRAFLOAD_100 +5.4E-03*ROADLENGTH_50	0.88	0.84	0.44	20	1.8 [0.47-4.1]
Belgium/ Netherlands	6.5 +4.8E-08*HDLDRES_5000 +5.0E-07*TRAFMAJORLOAD_50 +1.0E-02*MAJORROADLENGTH50 -6.7E-06*XPLUSY	0.83	0.81	1.15	40	5.0 [1.5-12]
Spain, Barcelona	-7.1 +6.9E-07*PORT_5000 +2.6E-05*HHOLD_5000 +1.9E-08*TRAFMAJORLOAD_500 +4.5E-06*TRAFLOAD_25	0.78	0.71	3.10	20	11 [3.0-25]
Fe						
Finland, Helsinki	72.1 -1.6E-06*GREEN_5000L +3.6E-01*HHOLD_100L +8.0E-02*ROADLENGTH_100	0.76	0.63	23.79	20	75 [15-169]
Belgium/ Netherlands	149.0 +1.4E-06*HDLDRES_5000 +1.9E-03*TRAFNEAR +8.7E-06*TRAFMAJORLOAD_50 -1.5E-04*XPLUSY	0.78	0.73	32.44	40	120 [33-278]
Spain, Barcelona	96.8 +2.2E-04*HDRES_500 +1.5E+03*DISTINVMAJOR1	0.69	0.63	66.96	20	236 [79-488]
K						
Finland, Helsinki	125.6 -8.0E-05*GREEN_500L	0.15	0.09	20.30	20	113 [78-151]
Belgium/ Netherlands	155.0 +3.5E-07*TRAFMAJORLOAD_300 +1.4E-04*XMINUSY	0.31	0.25	18.85	40	119 [76-167]
Spain, Barcelona	305.1 -3.8E-05*URBGREEN_300_1000 -1.9E-05*URBGREEN_1000_5000 -3.7E-04*URBGREEN_300 -3.2E-06*NATURAL_5000 +2.5E-06*TRAFLOAD_100 +5.7E-03*MAJORROADLENGHT_500	0.83	0.73	19.53	20	175 [111-254]

Table S1 continued

Study area	LUR model [1]	R^2 of model	R^2 validation	RMSE (validation) (ng/m^3) [2]	Number of sites	Measured concentration (ng/m^3) [3]
Ni						
Finland, Helsinki	0.7 +5.1E-06*POP_5000L	0.18	0.08	0.81	20	1.4 [0.18-3.1]
Belgium/ Netherlands	3.7 +8.6E-08*PORT_5000 -1.2E-05*XCOORD	0.76	0.72	0.54	40	2.3 [0.61-4.5]
Spain, Barcelona	6.3 -1.2E-07*GREEN_5000	0.60	0.55	1.00	20	4.4 [2.1-7.4]
S						
Finland, Helsinki	684.2 -6.4E-04*URBNATURAL_300L	0.31	0.23	50.98	20	649 [520-758]
Belgium/ Netherlands	1240.0 +1.1E-02*POP_500 -8.5E-04*YCOORD	0.32	0.27	110.51	40	915 [448-1107]
Spain, Barcelona	787.2 +1.5E-05*PORT_5000 +3.5E-02*HHOLD_300 +1.7E-07*TRAFLOAD_1000	0.67	0.58	70.11	20	1042 [821-1245]
Si						
Finland, Helsinki	86.2 -1.1E-03*URBNATURAL_100L +3.0E-01*HHOLD_100L +1.3E-06*TRAFLOAD_300	0.74	0.72	27.53	20	112 [17-209]
Belgium/ Netherlands	146.0 +2.6E-03*TRAFNEAR -1.1E-04*xplusy	0.46	0.39	39.09	40	101 [38-285]
Spain, Barcelona	-33.9 +5.1E-04*INDUSTRY_500 +1.1E-01*HHOLD_100 +3.1E-04*HHOLD_100_5000	0.48	0.35	37.72	20	181 [106-281]
V						
Finland, Helsinki	1.5 +4.5E-06*POP_5000L +7.3E-03*HHOLD_100L	0.47	0.30	0.85	20	2.5 [0.82-4.7]

Table S1 continued

Belgium/ Netherlands	5.6 +2.0E-07*PORT_5000 -1.8E-05*XCOORD	0.68	0.63	1.16	40	3.7 [1.3-9.0]
Spain, Barcelona	1.5 +8.4E-07*PORT_5000 +9.0E-04*ROADLENGHT_300	0.61	0.48	2.60	20	9.5 [2.6-17]
Study area	**LUR model [1]**	**R^2 of model**	**R^2 validation**	**RMSE (validation) (ng/m^3) [2]**	**Number of sites**	**Measured concentration (ng/m^3) [3]**
Zn						
Finland, Helsinki	17.9 -3.0E-06*GREEN_1000L	0.21	0.16	2.21	20	16 [12-19]
Belgium/ Netherlands	85.6 +2.0E-07*TRAFMAJORLOAD_300 +2.0E-04*XMINUSY	0.66	0.58	11.19	40	28 [13-87]
Spain, Barcelona	-9.7 +4.6E-06*INDUSTRY_5000 +3.4E-08*TRAFLOAD_1000 +1.0E+03*DISTINVHARBOUR	0.77	0.73	11.13	20	58 [28-101]

1 The following predictors were derived for all sites: the surface area (m^2) of high density residential land (HDRES_X), low density residential land (LDRES_X), all residential land (HLDRES_X), industry (INDUSTRY_X), port (PORT_X), urban green space (URBGREEN_X), natural land (NATURAL_X), urban green and natural land combined (GREEN_X), water (WATER_X), the number (N) or surface area (m^2) of buildings (BUILDINGS_X), population (N) (POP_X) or number (N) of households (HHOLD_X), the square root of altitude (SQRALT), a regional concentration estimate (µ /m3 o 10−5m−1), X-coordinate (XCOORD), Ycoordinate (YCOORD), total length (m) of all road and all major road segments (ROADLENGTH_X, MAJORROADLENGTH_X), inverse distance (m^{-1}) and inverse squared distance (m^{-2}) to the nearest road of the central road network (DISTINVNEARC1, DISTINVNEARC2) and the nearest major road in the central network (DISTINVMAJORC1, DISTINVMAJORC2), traffic intensity on the nearest road (TRAFNEAR) and nearest major road (TRAFMAJOR), heavy traffic intensity on the nearest road (HEAVYTRAFNEAR) and nearest major road (HEAVYTRAFMAJOR), inverse distance (m^{-1}) and inverse squared distance (m^{-2}) to the nearest road of the local network (DISTINVNEAR1, DISTINVNEAR2) and the nearest major road in the local network (DISTINVMAJOR1, DISTINVMAJOR2), the product of inverse/inverse squared distance to the nearest road and the traffic intensity on this road c * $-1m^{-1}$/ c * $-1m^{-2}$) (INTINVDIST, INTINVDIST2), equivalent for major roads (INTMAJORINVDIST, INTMAJORINVDIST2), and for heavy traffic (HEAVYINTINVDIST, HEAVYINTINVDIST2), the sum of (traffic intensity × the length of all road segments) within a buffer (c *−1*m) for all roads (TRAFLOAD_X), for major roads (TRAFMAJORLOAD_X), for heavy traffic (HEAVYTRAFLOAD_X) and heavy traffic on major roads (HEAVYTRAFMAJORLOAD_X. X is the size of the buffer (e.g. 100, 300, 500, 1000 and 5000 m for land use)

2 RMSE = root mean squared error

3 Mean (min – max)

Quality control

The concentrations, in ng/m^3, were calculated using the analyzed concentration minus the city-specific mean blank concentration divided by the sampled volume and multiplied by the exposed filter area.

$$CC_i = 7.8*(C_i\text{-}MBL)/V_s *1000 \quad (1)$$

Equation (1): calculation of the concentrations. Where CC_i is the calculated concentration for the sample i (ng/m^3), 7.8 is the exposed filter area (cm^2), C_i is the analyzed concentration for sample i (µg/cm^2). MBL is the mean blank concentration (µg/cm^2) and V_s is the sampled volume in m^3

For most of the elements modeled by ESCAPE, more than 75% of the samples exceeded the detection limit (Table S2). For zinc (Zn) this percentage was somewhat lower (69%). Most of the Zn samples that did not exceed the detection limit were from Finland, which had a very high dl for Zn. When the blank filter from Finland with lab number 10744 was not included, none of the samples were below the detection limit. The high blank measurement from Finland (number 10744) was excluded in all analyses.

Field duplicates were applied to calculate the precision of measurements expressed as coefficient of variation (CV).

$$CV = \frac{\sqrt{\frac{\sum_{i=1}^{n}(S_i - D_i)^2}{2*n}}}{\frac{\sum_{i=1}^{n}(S_i + D_i)}{2*n}} *100\% \quad (2)$$

Equation (2): Calculation of coefficient of variation. Where n is the number of duplicates and i is the sampling round (1 to n). S is the concentration of sample i and D is the concentration of corresponding duplicate I.[2]

The coefficients of variance (CV) for the duplicate measurements including the personal duplicate measurements are shown in Table S3. CV values for the elements were higher than the CV values for $PM_{2.5}$ mass and soot.[3] CV values were also substantially higher than the corresponding values in ESCAPE. In ESCAPE, CV values were below 10% for S, Cu and Fe. The same laboratory was used in VE^{3}SPA and ESCAPE. Differences include the sampler and indoor + outdoor samples in VE^{3}SPA versus outdoor in ESCAPE. Sample volumes were similar (20 vs 25 m^3). A CV value of 30% will lead to an uncertainty of the average concentration of about 12% (assuming six samples to calculate the average). This is relatively small to the observed variability at the 15 homes (Table 2 main paper). Therefore, the impact of high CV values on the further analysis based on averages is probably limited.

Table S2 Detection limits (ng/m³) and the percentage of samples (%) exceeding the detection limit for the eight elements

	Detection Limit			Samples above Dl (%)
	Helsinki (n=16)	Utrecht (n=15)	Barcelona (n=15)	
Si	5.49	5.34	8.94	100
S	0.00	0.00	1.02	100
K	1.17	1.17	2.51	100
V	0.22	0.21	0.29	95
Fe	4.63	2.27	34.10	100
Ni	0.24	0.31	0.27	82
Cu	0.71	0.68	0.99	98
Zn	0.68	1.01	0.75	100*

N= number of field blanks used for the calculation of the detection limit
*1 extreme blank from Helsinki was excluded from the analysis. With that value the detection limit for Zn in Helsinki was 21.21 and 68% of the Zn samples exceeded the dl.

Table S3 Coefficient of Variance (%) for the Duplicate measurements

	CV		
	Helsinki (n=20)	Utrecht (n=18)	Barcelona (n=20)
Si	41.77	87.28*	170.59**
S	16.28	22.74	21.29
K	9.07	39.67	30.98
V	24.35	29.85	23.04
Fe	31.67	31.27	96.03
Ni	48.35	40.74	45.22
Cu	22.29	15.05	36.92
Zn	9.00	33.16	31.33

In Helsinki and Barcelona, the number of indoor duplicate measurements was 15 and for Utrecht the number was 13, including the 5 personal duplicates that makes a total of 20 (or 18 for Utrecht) used for the calculation of the CV values.
*27.99 if the duplicate measurement at the reference site at 01-03-2012 was not included
**41.12 if the filters with number 11050 and 11052 are not included

Table S4 The median slopes (β) per country of the relationship between the outdoor measurements and the personal/indoor measurements per participant.

	Helsinki		Utrecht		Barcelona		Pooled	
Component	indoor	personal	indoor	personal	indoor	personal	indoor	personal
$PM_{2.5}$	0.38	0.60	0.41	0.44	0.59	0.64	0.48	0.48
Soot	0.49	0.42	0.68	0.66	0.62	0.40	0.66	0.47
Cu	-0.58	-0.93	0.53	0.32	0.64	0.61	0.48	0.04
Fe	0.41	0.29	0.56	0.40	0.46	0.80	0.50	0.40
K	0.39	0.36	0.94	0.76	0.74	0.73	0.74	0.69
Ni	0.43	0.47	0.68	0.66	0.84	0.72	0.68	0.63
S	0.79	0.67	0.85	0.77	0.85	0.87	0.81	0.74
Si	0.51	0.33	0.70	0.65	0.52	0.40	0.54	0.39
V	0.58	0.69	0.76	0.76	0.83	0.64	0.74	0.70
Zn	0.67	0.38	0.62	0.66	0.65	0.53	0.65	0.54

Indoor/outdoor and personal/outdoor concentration Ratios

The indoor/outdoor and personal/outdoor concentration ratios were calculated for all measurements, unadjusted for the reference site. The median, the 90% and the 95% percentiles are presented in table S5. The median ratio's for Cu were higher than 1 for Cu in Helsinki and Utrecht, suggesting that indoor sources are important for this element.

Table S5 The indoor/outdoor and personal/outdoor concentration ratios. The median, the 90% (p90) and the 95% (p95) percentiles are shown.

Indoor/	Helsinki			Utrecht			Barcelona		
Outdoor	Median	p90	p95	Median	p90	p95	Median	p90	p95
Cu	2,19	11,19	12,86	1,25	3,27	4,13	0,89	2,12	2,53
Fe	0,55	0,82	0,97	0,68	0,96	1,03	0,67	1,41	1,83
K	0,88	1,54	3,39	1,07	2,49	3,80	0,90	1,22	1,51
Ni	0,57	1,23	1,31	0,81	1,52	2,05	0,79	1,28	1,40
S	0,65	0,93	0,98	0,77	0,98	1,09	0,79	1,24	1,44
Si	0,89	2,27	2,98	1,17	3,49	4,65	1,05	3,26	4,28
V	0,59	1,02	1,18	0,77	1,45	1,81	0,77	1,27	1,46
Zn	0,62	0,94	1,05	0,79	1,05	1,24	0,74	1,18	1,31
Personal/	**Helsinki**			**Utrecht**			**Barcelona**		
Outdoor	**Median**	**p90**	**p95**	**Median**	**p90**	**p95**	**Median**	**p90**	**p95**
Cu	2,36	10,54	14,93	1,09	2,76	4,33	1,08	3,77	4,32
Fe	0,87	1,76	2,33	0,72	1,21	1,42	1,07	7,90	11,37
K	0,95	1,72	2,24	1,07	1,95	2,84	1,08	3,61	4,83
Ni	0,56	1,31	1,79	0,78	2,01	6,30	0,85	2,21	2,87
S	0,62	0,90	0,96	0,76	1,00	1,48	0,84	1,45	1,88
Si	1,07	3,18	3,86	1,37	4,30	5,00	2,24	12,33	17,21
V	0,59	1,00	1,17	0,74	1,08	1,53	0,82	1,48	1,92
Zn	0,68	1,06	1,45	0,80	1,26	1,71	0,82	1,84	2,60

Table S6 Ratio of average outdoor, indoor and personal concentrations at traffic and urban background locations relative to suburban background locations. Data for the three cities combined.

		Outdoor		Indoor		Personal	
Component	Site Type	Ratio	p	Ratio	p	Ratio	p
$PM_{2.5}$	traffic	1.15	0.38	1.27	0.21	0.96	0.86
	urban	0.97	0.85	1.08	0.68	0.98	0.94
Soot	traffic	1.51	0.02	1.65	0.02	1.34	0.13
	urban	1.04	0.82	1.22	0.33	1.15	0.48
Cu	traffic	2.15	0.00	1.54	0.05	1.20	0.44
	urban	1.23	0.41	1.17	0.49	1.12	0.61
Fe	traffic	2.08	0.00	1.26	0.39	1.16	0.69
	urban	1.23	0.27	1.28	0.32	1.00	0.99
K	traffic	1.03	0.84	1.32	0.20	1.06	0.80
	urban	0.96	0.74	1.02	0.94	0.96	0.84
Ni	traffic	1.13	0.65	1.21	0.52	1.17	0.62
	urban	0.99	0.97	0.88	0.65	0.98	0.96
S	traffic	0.86	0.17	0.99	0.97	1.03	0.87
	urban	0.91	0.40	1.04	0.80	1.00	0.99
Si	traffic	1.28	0.04	1.06	0.80	0.95	0.87
	urban	1.16	0.20	1.01	0.97	0.97	0.92
V	traffic	0.81	0.29	0.90	0.69	1.19	0.59
	urban	0.92	0.66	1.07	0.79	1.21	0.56
Zn	traffic	1.05	0.87	1.18	0.64	0.92	0.80
	urban	1.09	0.75	1.24	0.54	1.16	0.68

Regression Plots

Figure S1 Regression plots of the modeled concentrations versus measured concentrations for Cu and K (ng/m³).

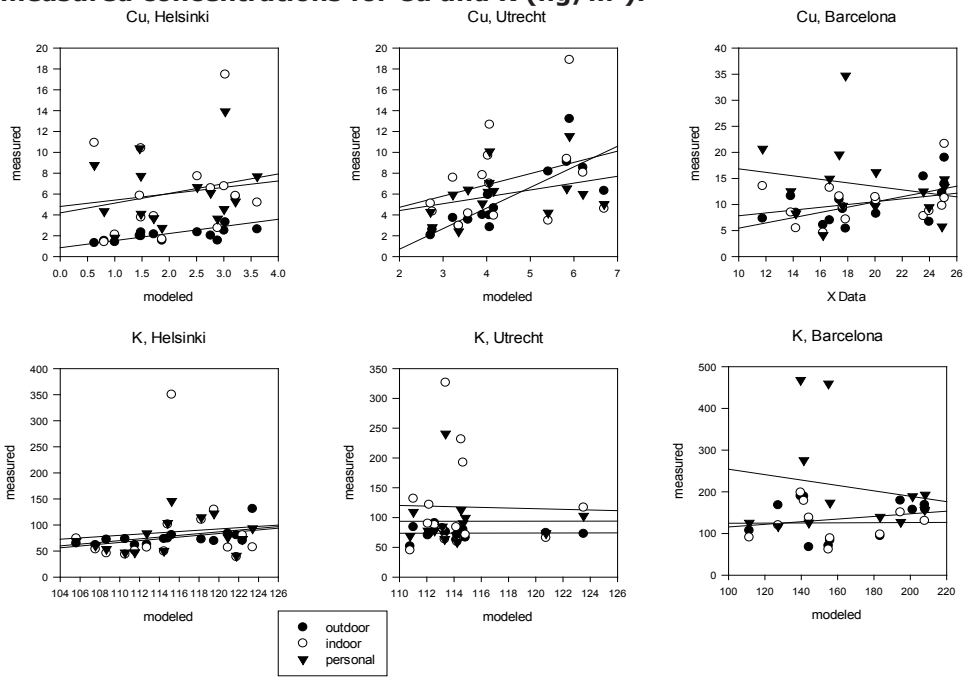


Figure S2 Regression plots of the modeled concentrations versus measured concentrations for Ni and Si (ng/m³).

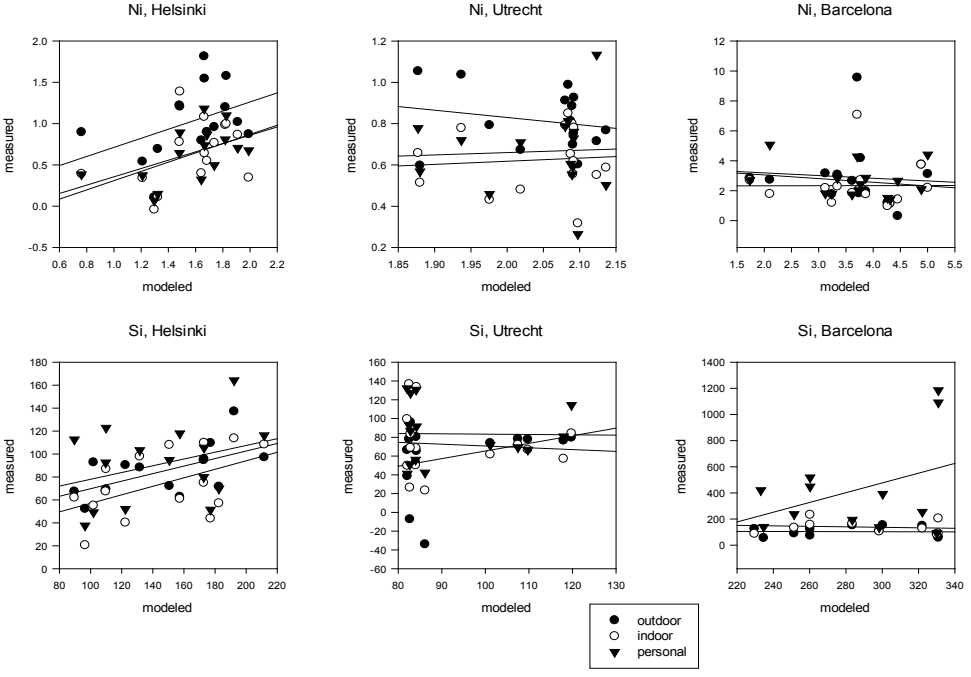
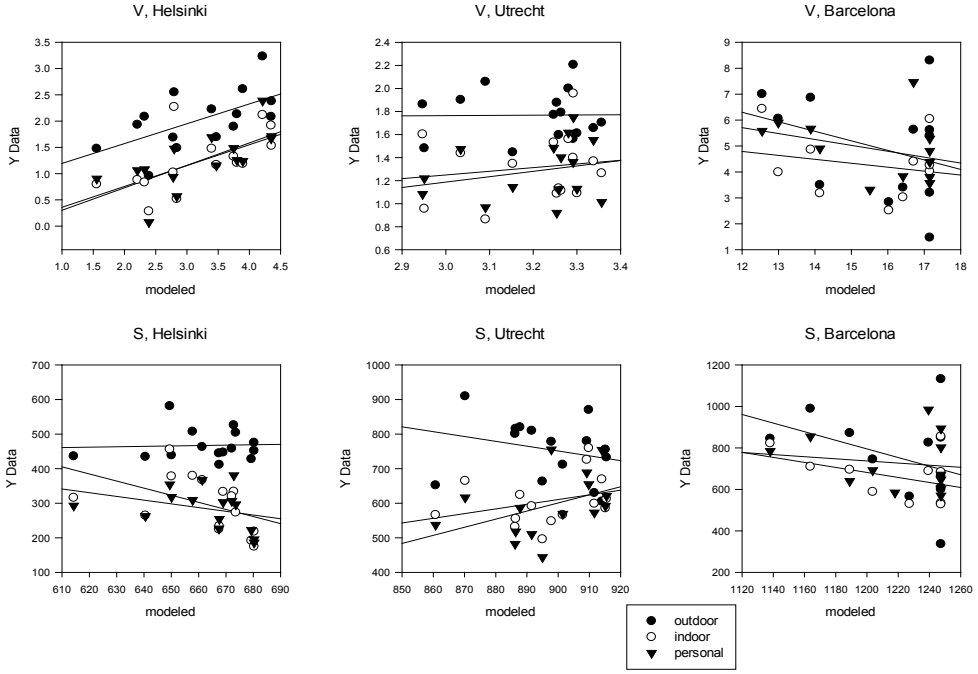


Figure S3 Regression plots of the modeled concentrations versus measured concentrations for V and S (ng/m³).



Regression Plots Pooled data

Figure S4 Regression plots of the pooled modeled concentrations versus measured concentrations for Cu and K (ng/m³).

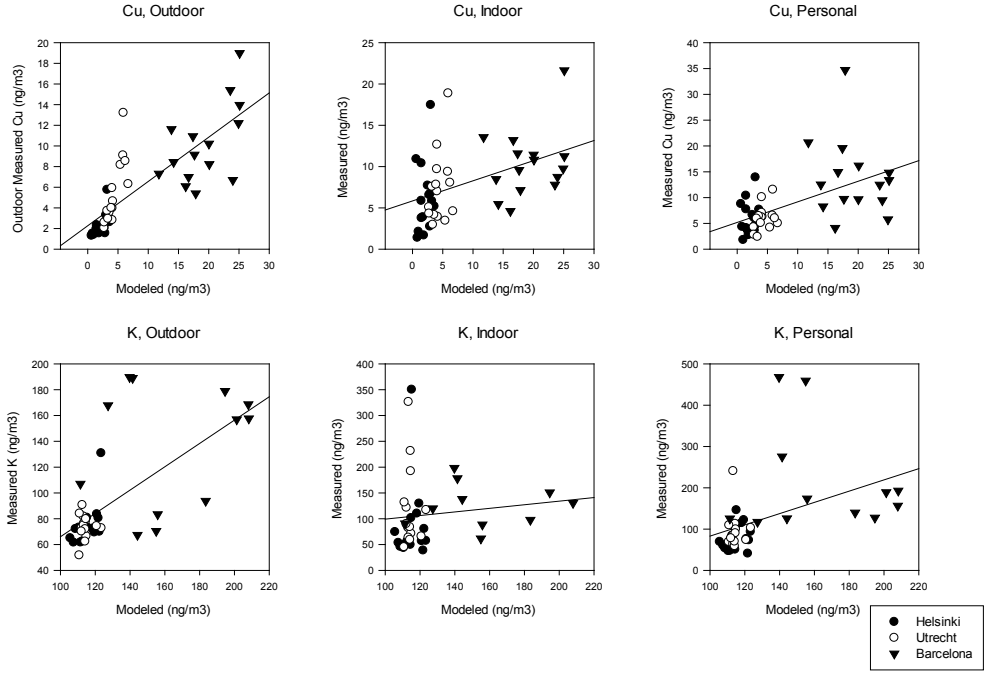


Figure S5 Regression plots of the pooled modeled concentrations versus measured concentrations for Ni and Si (ng/m³).

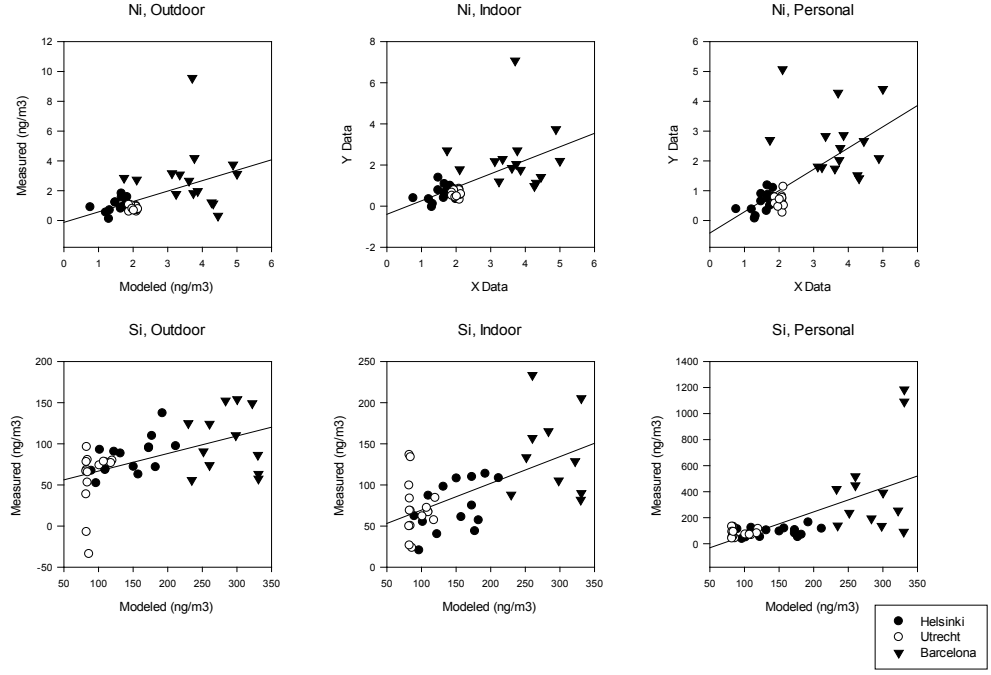
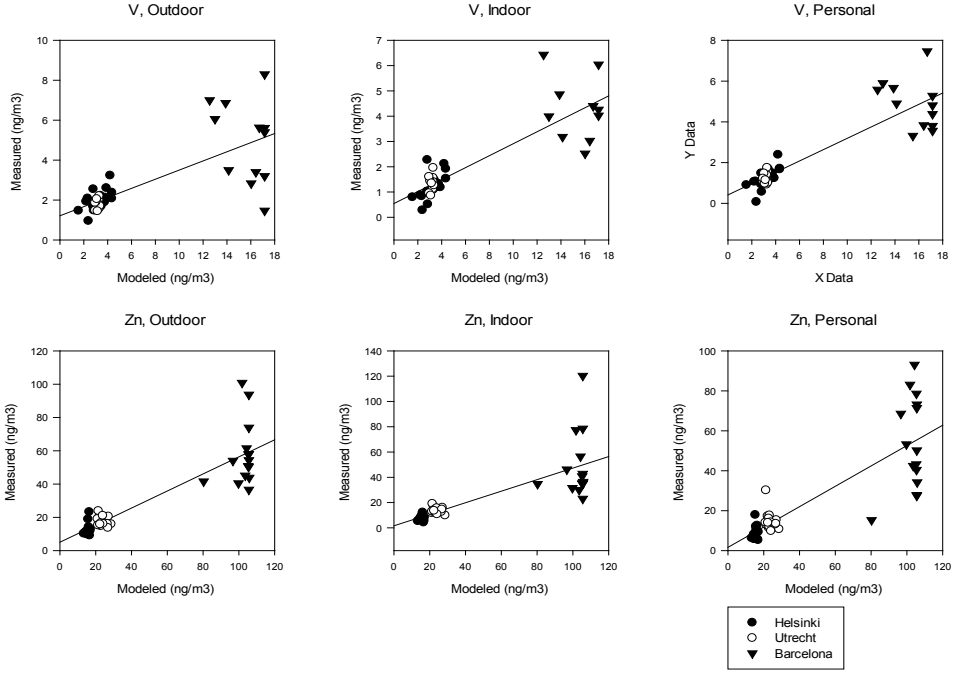


Figure S6 Regression plots of the pooled modeled concentrations versus measured concentrations for V and Zn (ng/m³).

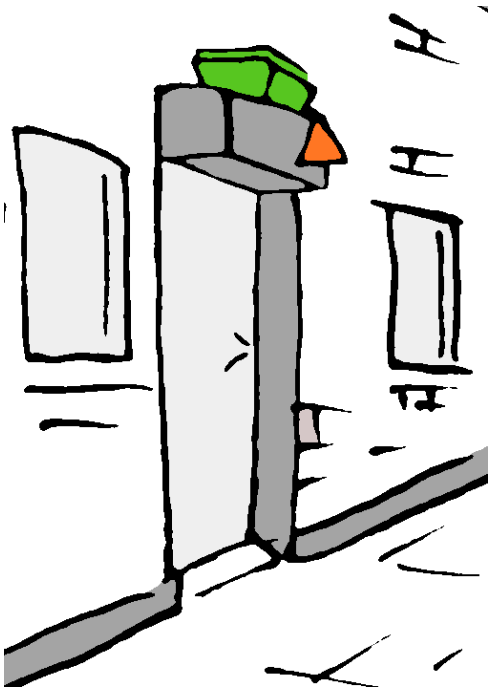


References

1. De Hoogh, K.; Wang, M.; Adam, M., et al Development of land use regression models for particle composition in twenty study areas in Europe. *Environ. Sci. Technol.* **2013,** *47,* 5778-5786.

2. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric Environment* **2012,** *62,* 303-317.

3. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Agreement of land use regression models with personal exposure measurements of particulate matter and nitrogen oxides air pollution. *Environ. Sci. Technol.* **2013,** *47,* 8523-8531.



Chapter 4

Temporal associations of ambient $PM_{2.5}$ elemental concentrations with indoor and personal concentrations

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Abstract

Time series studies increasingly evaluate health relevance of the elemental composition of particles smaller than 2.5 µm ($PM_{2.5}$). Validation studies have documented that temporal variation of outdoor $PM_{2.5}$ concentration is correlated with temporal variation of personal exposure, but very few papers have investigated the temporal correlation between outdoor concentration and personal exposure for the elemental composition of $PM_{2.5}$. We evaluated the temporal association between outdoor concentration and personal exposure for the elements copper (Cu), zinc (Zn), iron (Fe), potassium (K), nickel (Ni), vanadium (V), silicon (Si) and sulfur (S) in three European cities.

In Helsinki (Finland), Utrecht (the Netherlands) and Barcelona (Spain) five participants from urban background, five from suburban/rural background and five from busy street sites were selected (15 participants per city). Six outdoor, indoor and personal 96-hour average $PM_{2.5}$ concentrations were measured simultaneously in three different seasons (winter, summer and spring/autumn). Concurrently, samples were collected at a central reference site, reflecting urban background air pollution levels. The temporal variation at the central site was highly correlated with personal exposure for all elements, except Cu. The highest correlations (Pearson's R) were found for S and V (R between 0.87 and 0.98). Lower correlations were found for the elements Cu, Fe and Si associated with non-tailpipe traffic emissions and road dust (Pearson's R between -0.34 and 0.79). For $PM_{2.5}$ mass the R was lower (between 0.37 and 0.70). Exclusion of observations most affected by indoor sources increased the personal to central site correlations but did not fully explain differences between elements. The generally high correlation between temporal variation of the outdoor concentration and personal exposure supports the use of a central site for assessing exposure of PM components in time series studies for most elements. The different correlations found for the eight elements suggests that epidemiological associations are affected by differences in measurement error.

Introduction

Particulate matter with a diameter of less than 2.5 μm ($PM_{2.5}$) has been associated with adverse health effects. However, less is known about which constituents of $PM_{2.5}$ or which sources of particles are primarily responsible for these adverse health effects.[1-4] The ambient concentrations of these components vary temporally due to changes in weather and emissions. For many epidemiologic air pollution time series studies, a central monitoring site is used to determine the exposure of study subjects. Previous studies have shown that the ambient concentrations of $PM_{2.5}$ at a fixed site can be a good predictor for personal exposure, but the accuracy is dependent on the characteristics of participants, studies, and the environments in which they are conducted.[5] Very few papers have investigated the short term temporal correlations between outdoor and personal elemental concentrations of $PM_{2.5}$.[6] A study in Amsterdam and Helsinki found that with the exception of sulfur and PM absorbance as a measure of Black Carbon, longitudinal correlations between personal and outdoor Cu, Zn, Fe, K, Ni, V, Si and S elemental concentrations were less than the correlations for $PM_{2.5}$ which were 0.76 in Amsterdam and 0.74 in Helsinki.[6]

The aim of this paper is to assess the association between temporal variation in ambient concentrations of fine particle components at a central reference site and temporal variation in indoor and personal concentrations.

The study utilized repeated personal exposure measurements in Barcelona, Utrecht and Helsinki performed in the framework of the **V**alidation of **E**SCAPE **E**xposure **E**stimate**S** using **P**ersonal exposure **A**ssessment (VE^3SPA) project.[7] VE^3SPA was designed to evaluate how well land use regression models developed by the European Study of Cohorts for Air Pollution Effects (ESCAPE) project reflected spatial variation of outdoor, indoor and personal exposure.[8] The results for the spatial analyses have been published elsewhere for $PM_{2.5}$, NO_2 and soot (Montagne, 2013) and will be published elsewhere for the elemental composition.

Materials and Methods

Study design

$PM_{2.5}$, soot (light absorbance of $PM_{2.5}$ filters), NO_2 and NO_x were measured and the $PM_{2.5}$ filters samples were chemically analyzed for elemental composition. Eight trace elements were a priori selected to represent different sources of air pollution, copper (Cu), zinc (Zn), iron (Fe), potassium (K), nickel (Ni), vanadium (V), silicon (Si) and sulfur (S). These eight elements were the elements selected in ESCAPE for land use regres-

sion modeling and epidemiological analysis.[9] Cu, Zn and Fe are transition elements mainly associated with non-tailpipe traffic emissions and Fe is furthermore associated with heavy diesel emissions.[10,11] Potassium (K) is a marker for biomass burning and is moreover associated with road dust.[11,12] Nickel (Ni) and vanadium (V) are markers for fossil fuel combustion.[13] More than 80% of the Ni and 40% of Zn traffic emissions was estimated to be derived from exhaust emissions.[14] Additionally, silicon (Si) is a component of soil and sulfur (S) represents secondary sulfate from SO_2 emissions.

Standardized operating procedures for collecting samples were used in the three cities. The study manual can be found online (http://www.escape-project.eu/vespa/manual.php). In every city, 15 volunteers participated in this study. To increase the contrast in concentrations for the spatial evaluation, participants were selected from suburban background, urban background and busy street sites.

Sampling

The sampling design has been described in detail before.[7] Briefly, at every participant home address, 96- hour outdoor and indoor measurements were conducted. The 96 hour time period was chosen to have better representation of the yearly average concentration at the sites, which is important for the spatial analysis. Outdoor units were placed at the façade, for example on a balcony or hanging from a window, on the street side of the homes (>2 meters height) and indoor units in the living room on at least 1 m height. Simultaneously, personal exposure was measured with the sampling equipment placed in backpacks carried by the participants. NO_2 samples were collected using Ogawa diffusion badges (Ogawa & Company USA Inc., Pompano Beach Florida). $PM_{2.5}$ samples were collected on Teflon filters using BGI GK2.05SH cyclones and BGI 400 pumps (BGI inc., Waltham, Massachusetts) personal pump units. The same equipment and methods were applied for all measurement types and in all three cities. The participants followed two pre-described time activity patterns designed to represent the groups most sensitive for air pollution, one represented school going children and the other elderly, retired people. The 96- hour samples were taken from Monday to Friday, two weeks in a row and during warm, cold and intermediate seasons. Thus, we had 6 outdoor, 6 indoor and 6 personal samples per participant. The study period ran from 01-03-2010 to 28-03-2011. Sampling was conducted by three participants synchronously, two from background sites and one from a busy street location. During the whole measurement campaign samples were taken at a background central site in each city, concurrent with the samples at the participant homes. Samples were excluded if the unit had run less than 60% of the target of 96 hours and/or if the end flow of the pump unit was not within 35% of 3.5 l/m.

Site description

The description of participant homes can be found elsewhere.[7] Briefly, in Utrecht, 20% of the living rooms were situated higher than on the second floor, compared to 40% in Helsinki. In Barcelona, none of the living rooms were on the ground floor and around 47% were higher than the second floor. Furthermore, 60%, 40% and 0% of the homes in Utrecht, Helsinki and Barcelona had an open kitchen, respectively.

Sample analysis

Ogawa badges were analyzed with a spectrophotometer based upon the Saltzman method[15], following ESCAPE procedures.[16] After the Teflon filters were weighted to determine $PM_{2.5}$ concentrations at the IRAS laboratory in Utrecht, the samples were transported to Cooper Environmental Services (Portland, Oregon, USA). During transport, the filters were cooled. The filters were analyzed by energy dispersive x-ray fluorescence (ED-XRF) spectrometry to quantify the concentration of metals of these samples.[9] Filters were analyzed between October 2011 and February 2012. Quality assurance and control included analysis of NIST reference material (SRM 1228 and SRM 987), repeated analysis of a multi-elemental quality control standard (Multi 30585) and replicate analysis of about 10% of the samples. All analyzed batches passed the quality criteria of the laboratory. In addition, about 15 field blanks, 15 outdoor/indoor duplicates and 5 personal duplicates were taken in each city. The mean field blank per city was determined and the detection limit (DL) per city was calculated as three times the standard deviation of the field blanks divided by the nominal sample volume of 20.2 m^3. Field duplicates were applied to calculate the precision of measurements expressed as coefficient of variation (CV). The equation for the CV can be found in the online supplements (online supplement 1, OLS 1).
The concentrations, in ng/m^3, were calculated using the analyzed concentration minus the city-specific mean blank concentration divided by the sampled volume and multiplied by the exposed filter area.

Data analysis

The concentrations at the central reference site were compared to the simultaneously measured indoor and personal concentrations. Because we were interested in temporal associations, we performed individual regression analyses with the six measurements per participant, following previous studies.[17,18] Next, the median of these 15 correlation coefficients (Pearson's R) per country was determined. For further interpretation, the agreement of the concentrations at the central site with the home outdoor and of the home outdoor measurements with the indoor and personal concentrations was determined in the same manner. The analyses with

the central site concentrations are our primary analyses, as epidemiological time series studies are often based upon central site measurements. We interpret both correlations and the regression slopes, particularly the indoor-outdoor slopes. Regression slopes have been used to represent infiltration factors with the intercept reflecting indoor sources contributions.[19] The measurements at the central site had some missing data in Utrecht and especially Barcelona. Some of this missing data was imputed using central site data from other institutes (online supplement 2, OLS 2). In additional analyses, the busy street sites and the background sites were assessed separately (online supplement 3, OLS 3). Furthermore, the associations of outdoor NO_2 and $PM_{2.5}$ concentrations with the outdoor/indoor/personal concentrations of the eight elements were determined (OLS 4).

Indoor/outdoor and personal/outdoor ratios were determined per sample to assess the impact of indoor sources (OLS 5 Table S4). Additional analyses were performed where the samples with ratios>1.5 or ratios>2 were excluded (Table 7 and OLS 5 Table S5), to remove samples where indoor sources were influential. The rationale for these analyses is that for epidemiological time series studies, the most relevant correlation is between central site concentration and the personal/indoor exposure from outdoor origin, which is however difficult to quantify.[20] Regression analyses were performed with SAS, version 9.2.

Table 1 Detection limits (ng/m³) and the percentage of samples (%) exceeding the detection limit for the different elements.

	Detection Limit			Samples above Dl (%)
	Helsinki (n=16)	Utrecht (n=15)	Barcelona (n=15)	
Si	5.49	5.34	8.94	100
S	0.00	0.00	1.02	100
K	1.17	1.17	2.51	100
V	0.22	0.21	0.29	95
Fe	4.63	2.27	34.10	100
Ni	0.24	0.31	0.27	82
Cu	0.71	0.68	0.99	98
Zn	0.68	1.01	0.75	100*

N= number of field blanks used for the calculation of the detection limit
*1 extreme blank from Helsinki was excluded from the analysis. With that value the detection limit for Zn in Helsinki was 21.21 and 68% of the Zn samples exceeded the dl.

Results

Quality control

For most elements, more than 75% of the samples exceeded the detection limit (Table 1). For zinc (Zn) this percentage was slightly lower (68%), but was 100% if one extreme blank was excluded. This high blank measurement was excluded in all analyses. The coefficients of variance (CV) for the duplicate measurements, including the personal duplicate measurements, are shown in Table 2. CV values were fairly high, often exceeding 20%.

Table 2 Coefficient of Variance (%) for the Duplicate measurements

	CV		
	Helsinki (n=20)	**Utrecht (n=18)**	**Barcelona (n=20)**
Si	41.77	87.28*	170.59**
S	16.28	22.74	21.29
K	9.07	39.67	30.98
V	24.35	29.85	23.04
Fe	31.67	31.27	96.03
Ni	48.35	40.74	45.22
Cu	22.29	15.05	36.92
Zn	9.00	33.16	31.33

In Helsinki and Barcelona, the number of indoor and outdoor duplicate measurements was 15 and for Utrecht the number was 13, including the 5 personal duplicates that makes a total of 20 (or 18 for Utrecht) used for the calculation of the CV values.
*27.99 if the duplicate measurement at the central site at 01-03-2012 was not included
**41.12 if the filters with number 11050 and 11052 (personal duplicate measurements) are not included. Filter 11052 had visible fluff on the filter, we have no explanation for the other filter.

Descriptive Results

The median, first and third quartile concentrations for the components are shown in Table 3. The highest mean concentrations were observed for S and next for Si, K and Fe. A large range in concentrations was found within each city. For most components, the concentrations at the central site were higher than the personal concentrations but lower than the outdoor concentrations measured at the homes. For Si, K and especially Cu, indoor and personal concentrations were higher than the outdoor concentrations measured at the homes, except for indoor Si in Helsinki and indoor K in Barcelona.

Table 3 The median and the first and third quartiles (Q1 - Q3) concentrations for $PM_{2.5}$ (μg/m³), soot ($m^{-1}x10^{-5}$), NO_2 (μg/m³), and the eight elements (ng/m3) at the central site, the outdoor, indoor and personal sites in Helsinki, Utrecht and Barcelona.

	Central		Outdoor		Indoor		Personal	
Component	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)
				Helsinki				
$PM_{2.5}$	6.9	(4.1 - 9.3)	6.4	(4.6 - 8.4)	5.2	(3.8 - 8.3)	5.2	(3.8 - 7.9)
Soot	0.7	(0.7 - 1.1)	0.8	(0.6 - 1.1)	0.6	(0.4 - 0.8)	0.7	(0.5 - 0.8)
NO_2	23.6	(19.2 - 36.4)	21.1	(16.2 - 31.2)	12.6	(8.3 - 20.2)	16.2	(12.2 - 21.3)
Cu	2.1	(1.7 - 2.8)	1.7	(1.3 - 3.0)	4.4	(1.9 - 9.6)	4.2	(2.6 - 8.3)
Fe	7.5	(4.8 - 12.8)	8.8	(4.6 - 13.1)	3.8	(2.4 - 6.6)	4.5	(2.9 - 7.9)
K	55.2	(44.3 - 91.1)	54.0	(35.7 - 85.0)	29.0	(15.6 - 43.4)	44.1	(29.9 - 74.7)
Ni	61.2	(42.0 - 81.7)	58.5	(40.7 - 93.5)	51.7	(41.0 - 74.5)	56.9	(40.2 - 84.4)
S	0.9	(0.5 - 1.8)	0.7	(0.4 - 1.4)	0.4	(0.2 - 0.9)	0.4	(0.2 - 0.9)
Si	1.9	(0.8 - 3.2)	1.5	(0.8 - 2.6)	0.9	(0.3 - 1.6)	0.9	(0.3 - 1.8)
V	61.4	(36.4 - 127.6)	63.3	(35.5 - 111.2)	56.3	(32.3 - 92.5)	77.5	(43.4 - 105.6)
Zn	413.3	(254.1 - 620.3)	401.5	(257.6 - 639.7)	229.1	(136.1 - 398.7)	216.3	(142.0 - 428.8)
				Utrecht				
$PM_{2.5}$	11.4	(8.0 - 17.3)	15.2	(10.6 - 20.4)	11.2	(7.6 - 14.9)	10.9	(7.3 - 15.1)
Soot	0.9	(0.7 - 1.2)	1.3	(0.9 - 1.7)	1.0	(0.7 - 1.3)	1.0	(0.8 - 1.3)
NO_2	22.7	(18.5 - 28.3)	33.5	(23.3 - 42.1)	21.6	(16.8 - 30.4)	24.3	(18.0 - 28.1)
Cu	3.1	(2.1 - 3.8)	4.4	(2.8 - 6.2)	5.2	(3.6 - 8.6)	4.8	(3.4 - 6.9)
Fe	14.0	(8.7 - 17.3)	17.1	(10.5 - 23.1)	12.7	(9.2 - 18.8)	12.4	(9.3 - 18.5)
K	74.6	(51.0 - 115.5)	112.1	(67.9 - 163.0)	71.4	(46.1 - 101.1)	80.7	(51.8 - 111.5)
Ni	65.2	(42.6 - 71.5)	71.4	(47.3 - 90.5)	79.5	(51.2 - 115.7)	74.4	(52.3 - 106.7)
S	0.6	(0.4 - 1.0)	0.7	(0.3 - 1.1)	0.6	(0.3 - 0.8)	0.5	(0.3 - 1.0)
Si	1.3	(0.9 - 2.1)	1.3	(0.9 - 2.4)	1.1	(0.6 - 1.6)	1.0	(0.6 - 1.5)
V	33.1	(16.8 - 76.4)	49.9	(30.9 - 70.6)	59.5	(42.0 - 94.1)	66.5	(44.3 - 100.6)
Zn	585.9	(322.0 - 776.5)	754.4	(482.7 - 955.8)	543.5	(376.5 - 745.4)	564.8	(384.6 - 761.6)
				Barcelona				
$PM_{2.5}$	16.1	(11.9 - 22.0)	15.7	(12.5 - 19.6)	14.3	(11.8 - 20.0)	19.4	(13.2 - 28.8)
Soot	1.7	(1.2 - 2.6)	2.4	(2.0 - 3.2)	2.1	(1.6 - 2.6)	2.2	(1.8 - 2.7)
NO_2	50.7	(39.8 - 72.5)	70.3	(56.5 - 84.3)	53.0	(42.6 - 60.0)	49.0	(41.9 - 59.3)
Cu	7.4	(4.5 - 10.7)	9.2	(6.8 - 12.8)	9.1	(5.9 - 12.9)	9.8	(7.5 - 18.5)
Fe	39.7	(21.6 - 73.3)	44.5	(26.4 - 72.0)	32.2	(20.0 - 57.5)	36.3	(23.5 - 69.4)
K	171.9	(105.0 - 257.3)	174.0	(119.0 - 244.9)	123.6	(74.8 - 173.0)	186.1	(97.1 - 467.2)
Ni	157.7	(118.6 - 339.0)	110.3	(76.1 - 152.1)	97.3	(73.6 - 147.4)	129.1	(89.1 - 246.2)
S	2.6	(1.4 - 4.7)	2.0	(1.1 - 3.2)	1.7	(0.9 - 2.9)	1.9	(0.9 - 3.8)
Si	5.6	(3.0 - 10.0)	4.3	(2.8 - 6.8)	3.5	(2.2 - 6.6)	3.8	(1.9 - 7.7)
V	100.8	(73.2 - 230.6)	80.1	(53.8 - 124.4)	98.3	(67.7 - 139.7)	173.7	(90.7 - 358.7)
Zn	597.2	(400.0 - 1287.2)	690.7	(417.1 - 1147.2)	603.4	(333.6 - 1034.0)	593.1	(308.8 - 1092.3)

Home outdoor $PM_{2.5}$ and NO_2 concentrations are temporally only moderately to barely correlated to the personal concentrations of the eight elements (OLS 4). Zn, V and S show moderate correlations with personal $PM_{2.5}$ (R ranging from 0.67-0.78) in Helsinki, while correlations for these elements were lower in Utrecht and Barcelona. In Utrecht, a higher correlation was found for Cu (R=0.77) and K (R=0.65). In Barcelona the highest correlation was found for Si (R=0.63).

Central site versus outdoor/indoor/personal

Table 4 shows the median correlation coefficients between the measurements at the central site and the home outdoor, indoor and personal measurements at the VE^{3}SPA sites. High correlations were found between the central site concentrations and the home outdoor concentrations for all components in Helsinki and Utrecht. High correlations were also found in Barcelona for the elements S and V, but especially for Cu, Fe and Si home outdoor concentrations showed more moderate correlations with the central site. Furthermore, in Helsinki and Utrecht lower correlations were found for Cu and Fe than for S.

The correlations of central site concentrations with personal and indoor concentrations were lower than with home outdoor concentrations. The personal concentrations were highly correlated (R>0.8) to the measurements at the central site for S and V in the three cities. Correlations for $PM_{2.5}$, soot, NO_2, Fe, K, Ni and Zn were moderate to high. The least consistent associations were found for Si and Cu. The personal and indoor Cu concentrations were not associated to the central site concentrations in Helsinki and neither was the personal Si concentration in Barcelona. An analysis stratified by site type, showed that central site personal exposure correlations were only moderately higher for background homes than for traffic homes (OLS 3). For soot the median central site personal exposure correlation was 0.76 and 0.71 for background and traffic homes respectively in the pooled dataset.
When the samples with indoor/outdoor ratios>2 or ratios>1.5 were excluded from the analysis, the median correlations with the indoor and personal concentrations, especially for Cu, were higher than for the main analysis (Table 7 and OLS 5 Table S5).

Individual correlation coefficients differed substantially between subjects (Table 4). A large fraction of this variation is likely random, as we have at most six observations per subject. Spending more or less than the median time at home did not explain variability of the individual correlation coefficients (OLS 6).

Following the child or elderly time activity pattern resulted in similar correlations between central site and personal exposure (OLS 6), e.g.

Table 4 The median, first and third quartiles (Q1 – Q3) of individual correlation coefficients (Pearson's R) of the measurements at the central site and the outdoor/indoor/personal measurements (of the participants with >2 measurements)

Outdoor		Helsinki		Utrecht		Barcelona		Pooled
Component	median	(Q1- Q3)	median	(Q1- Q3)	median	(Q1- Q3)	median	(Q1- Q3)
$PM_{2.5}$	0.88*	(0.83 - 0.97)	0.92*	(0.81 - 0.97)	0.79*	(0.60 - 0.90)	0.87*	(0.79 - 0.95)
Soot	0.90*	(0.71 - 0.93)	0.88*	(0.76 - 0.93)	0.72*	(0.45 - 0.91)	0.87*	(0.68 - 0.93)
NO_2	0.97*	(0.87 - 0.99)	0.92*	(0.80 - 0.97)	0.89*	(0.76 - 0.94)	0.92*	(0.82 - 0.97)
Cu	0.78*	(0.09 - 0.92)	0.75*	(0.24 - 0.85)	0.47*	(0.22 - 0.83)	0.19*	(-0.22 - 0.69)
Fe	0.78*	(0.51 - 0.90)	0.71*	(0.37 - 0.80)	0.54'	(-0.26 - 0.90)	0.65*	(0.12 - 0.85)
K	0.95*	(0.90 - 0.99)	0.92*	(0.85 - 0.94)	0.73*	(0.11 - 0.87)	0.69*	(0.22 - 0.90)
Ni	0.90*	(0.04 - 0.94)	0.86*	(0.61 - 0.96)	0.63*	(0.30 - 0.75)	0.77*	(0.20 - 0.89)
S	0.98*	(0.94 - 0.99)	0.91*	(0.77 - 0.95)	0.88*	(0.76 - 0.95)	0.93*	(0.80 - 0.97)
Si	0.90*	(0.76 - 0.98)	0.72*	(0.30 - 0.97)	0.48	(-0.24 - 0.76)	0.40*	(-0.14 - 0.73)
V	0.93*	(0.80 - 0.98)	0.95*	(0.91 - 0.98)	0.87*	(0.40 - 0.95)	0.91*	(0.67 - 0.97)
Zn	0.93*	(0.88 - 0.98)	0.91*	(0.73 - 0.97)	0.63*	(0.31 - 0.86)	0.80*	(0.41 - 0.90)
Indoor		**Helsinki**		**Utrecht**		**Barcelona**		**Pooled**
Component	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**
$PM_{2.5}$	0.45*	(0.16 - 0.90)	0.59*	(0.09 - 0.91)	0.58*	(0.47 - 0.84)	0.58*	(0.28 - 0.89)
Soot	0.75*	(0.38 - 0.91)	0.83*	(0.78 - 0.95)	0.56*	(0.38 - 0.87)	0.79*	(0.53 - 0.90)
NO_2	0.56	(-0.33 - 0.90)	0.50*	(-0.09 - 0.77)	0.41	(-0.52 - 0.73)	0.58*	(0.28 - 0.89)
Cu	-0.30	(-0.60 - 0.54)	0.31*	(0.09 - 0.65)	0.59*	(0.08 - 0.82)	0.31*	(-0.35 - 0.73)
Fe	0.79*	(0.49 - 0.90)	0.64*	(0.24 - 0.87)	0.57*	(0.09 - 0.77)	0.71*	(0.40 - 0.86)
K	0.66*	(0.24 - 0.91)	0.76*	(0.13 - 0.96)	0.57*	(0.10 - 0.77)	0.64*	(0.19 - 0.92)
Ni	0.71*	(-0.11 - 0.93)	0.88*	(0.70 - 0.94)	0.72*	(0.14 - 0.86)	0.81*	(0.30 - 0.91)

Table 4 continued

S	0.88*	(0.80 - 0.97)	0.85*	(0.70 - 0.98)	0.79*	(0.46 - 0.89)	0.85*	(0.75 - 0.97)
Si	0.80*	(0.68 - 0.96)	0.50*	(-0.02 - 0.86)	0.60	(-0.50 - 0.73)	0.69*	(0.07 - 0.86)
V	0.94*	(0.73 - 0.99)	0.91*	(0.72 - 0.97)	0.75*	(-0.03 - 0.93)	0.91*	(0.64 - 0.97)
Zn	0.89*	(0.57 - 0.95)	0.87*	(0.60 - 0.94)	0.61*	(0.21 - 0.85)	0.79*	(0.51 - 0.93)

Personal		**Helsinki**		**Utrecht**		**Barcelona**		**Pooled**
Component	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**	**median**	**(Q1- Q3)**
$PM_{2.5}$	0.70*	(0.13 - 0.87)	0.68*	(0.15 - 0.88)	0.37*	(0.09 - 0.72)	0.57*	(0.14 - 0.82)
Soot	0.68*	(0.30 - 0.91)	0.85*	(0.71 - 0.95)	0.62*	(0.12 - 0.79)	0.74*	(0.56 - 0.90)
NO_2	0.72*	(0.41 - 0.94)	0.73*	(0.60 - 0.90)	0.46*	(-0.13 - 0.79)	0.57*	(0.14 - 0.82)
Cu	0.02	(-0.42 - 0.40)	0.28*	(0.15 - 0.79)	0.22*	(-0.22 - 0.75)	0.19*	(-0.22 - 0.69)
Fe	0.50*	(0.33 - 0.83)	0.79*	(0.12 - 0.90)	0.51'	(0.06 - 0.76)	0.65*	(0.12 - 0.85)
K	0.70*	(0.27 - 0.80)	0.70*	(-0.11 - 0.90)	0.63*	(0.39 - 0.94)	0.69*	(0.22 - 0.90)
Ni	0.69*	(0.15 - 0.91)	0.88*	(0.68 - 0.94)	0.68*	(0.00 - 0.86)	0.77*	(0.20 - 0.89)
S	0.93*	(0.87 - 0.98)	0.90*	(0.43 - 0.98)	0.90*	(0.48 - 0.96)	0.93*	(0.80 - 0.97)
Si	0.70*	(0.38 - 0.87)	0.53*	(-0.14 - 0.71)	-0.34	(-0.63 - 0.27)	0.40*	(-0.14 - 0.73)
V	0.91*	(0.74 - 0.97)	0.91*	(0.66 - 0.98)	0.88*	(0.34 - 0.96)	0.91*	(0.67 - 0.97)
Zn	0.82*	(0.59 - 0.96)	0.80*	(0.39 - 0.91)	0.72*	(0.28 - 0.85)	0.80*	(0.41 - 0.90)

N=15 in Helsinki, Utrecht and Cu, Ni, Zn in Barcelona; n=12 for outdoor, n=10 for indoor and n=12 for personal Fe, K, S, Si and V concentrations in Barcelona. Outdoor (outd), indoor (ind) and personal (pers)
*significant at the p<0.05 level ` significant at the p<0.10 level

Table 5 The median, first and third quartiles (Q1 – Q3) correlation coefficients (Pearson's R) of the association between the home outdoor measurements and the personal/indoor measurements per participant, per city and pooled

Indoor		Helsinki		Utrecht		Barcelona		Pooled	
Component	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)
$PM_{2.5}$	0.51*	(0.07 - 0.92)	0.82*	(0.12 - 0.93)	0.79*	(0.52 - 0.92)	0.79*	(0.20 - 0.92)
Soot	0.79*	(0.67 - 0.96)	0.95*	(0.82 - 0.98)	0.81*	(0.65 - 0.96)	0.87*	(0.70 - 0.96)
NO_2	0.25*	(-0.46 - 0.91)	0.57*	(0.06 - 0.81)	0.48*	(0.00 - 0.82)	0.49*	(-0.02 - 0.82)
Cu	-0,14	(-0,60 - 0,24)	0,21*	(0,10 - 0,84)	0,48*	(0,29 - 0,85)	0,24*	(-0,11 - 0,71)
Fe	0,75*	(0,56 - 0,97)	0,87*	(0,64 - 0,93)	0,39*	(0,08 - 0,90)	0,75*	(0,48 - 0,92)
K	0,85*	(0,25 - 0,97)	0,89*	(0,54 - 0,95)	0,91*	(0,82 - 0,98)	0,89*	(0,54 - 0,96)
Ni	0,85*	(0,51 - 0,97)	0,86*	(0,64 - 0,96)	0,90*	(0,86 - 0,96)	0,88*	(0,71 - 0,96)
S	0,94*	(0,84 - 0,96)	0,97*	(0,94 - 0,99)	0,91*	(0,86 - 0,97)	0,95*	(0,88 - 0,98)
Si	0,81*	(0,45 - 0,96)	0,78*	(0,36 - 0,95)	0,50*	(0,20 - 0,81)	0,74*	(0,36 - 0,94)
V	0,94*	(0,73 - 0,96)	0,93*	(0,87 - 0,98)	0,96*	(0,89 - 0,98)	0,94*	(0,87 - 0,97)
Zn	0,94*	(0,47 - 0,98)	0,93*	(0,85 - 0,96)	0,97*	(0,78 - 0,98)	0,94*	(0,78 - 0,98)
Personal		**Helsinki**		**Utrecht**		**Barcelona**		**Pooled**
Component	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)
$PM_{2.5}$	0,67*	(0.11 - 0.86)	0.71*	(0.11 - 0.84)	0.41*	(0.27 - 0.82)	0.67*	(0.11 - 0.86)
Soot	0,72*	(0.41 - 0.91)	0.89*	(0.69 - 0.97)	0.67*	(0.47 - 0.95)	0.76*	(0.41 - 0.91)
NO_2	0,77*	(0.29 - 0.91)	0.77*	(0.69 - 0.89)	0.43*	(0.24 - 0.74)	0.73*	(0.29 - 0.91)
Cu	-0,30	(-0,50 - -0,18)	0,35'	(-0,11 - 0,88)	0,50*	(0,06 - 0,78)	0,06*	(-0,28 - 0,71)
Fe	0,46*	(-0,04 - 0,82)	0,70*	(0,45 - 0,91)	0,40*	(0,13 - 0,71)	0,54*	(0,13 - 0,85)
K	0,68*	(0,12 - 0,93)	0,86*	(0,42 - 0,92)	0,79*	(0,49 - 0,90)	0,79*	(0,45 - 0,92)
Ni	0,77*	(0,39 - 0,95)	0,72*	(0,61 - 0,90)	0,88*	(0,44 - 0,96)	0,78*	(0,61 - 0,95)
S	0,94*	(0,91 - 0,98)	0,95*	(0,76 - 0,98)	0,92*	(0,75 - 0,98)	0,94*	(0,87 - 0,98)
Si	0,60*	(0,19 - 0,80)	0,66*	(0,10 - 0,74)	0,28*	(-0,18 - 0,88)	0,58*	(-0,02 - 0,80)
V	0,92*	(0,82 - 0,97)	0,94*	(0,83 - 0,97)	0,95*	(0,83 - 0,97)	0,94*	(0,83 - 0,97)
Zn	0,78*	(0,52 - 0,99)	0,82*	(0,77 - 0,92)	0,88*	(0,55 - 0,98)	0,83*	(0,67 - 0,96)

N=15 per city and N=45 for the pooled analysis * significant at the p<0.05 level ' significant at the p<0.10 level

Table 6 The median and the first and third quartiles (Q1 – Q3) slopes (β) of the regression between the outdoor measurements and the personal/indoor measurements per participant, per city and pooled. $PM_{2.5}$ and NO_2 are in µg/m³, soot is in $m^{-1}x10^{-5}$ and the elements are in ng/m³.

Indoor	Helsinki		Utrecht		Barcelona		Pooled	
Component	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)
$PM_{2.5}$	0.38*	(0.11 - 0.88)	0.41*	(0.04 - 0.55)	0.59*	(0.32 - 0.72)	0.48*	(0.12 - 0.75)
Soot	0.49*	(0.34 - 0.92)	0.68*	(0.53 - 0.90)	0.62*	(0.43 - 0.87)	0.66*	(0.43 - 0.87)
NO_2	0.11*	(-0.09 - 0.54)	0.29*	(0.05 - 0.44)	0.20*	(0.00 - 0.71)	0.24*	(-0.01 - 0.52)
Cu	-0,57’	(-2,16 - 0,48)	0,53*	(0,12 - 1,18)	0,64*	(0,35 - 0,72)	0,48*	(-0,22 - 0,73)
Fe	0,41*	(0,24 - 0,73)	0,56*	(0,30 - 0,82)	0,46*	(0,06 - 0,68)	0,50*	(0,24 - 0,69)
K	0,39’	(0,21 - 0,81)	0,94*	(0,65 - 1,41)	0,74*	(0,60 - 1,01)	0,74*	(0,39 - 1,08)
Ni	0,43*	(0,29 - 0,77)	0,68*	(0,52 - 0,92)	0,84*	(0,65 - 0,96)	0,68*	(0,48 - 0,93)
S	0,79*	(0,40 - 0,96)	0,85*	(0,66 - 0,97)	0,85*	(0,64 - 0,94)	0,81*	(0,63 - 0,94)
Si	0,51*	(0,24 - 0,62)	0,70*	(0,36 - 0,82)	0,52	(0,18 - 0,85)	0,54*	(0,24 - 0,75)
V	0,58*	(0,35 - 0,83)	0,76*	(0,63 - 0,89)	0,83*	(0,61 - 1,01)	0,74*	(0,56 - 0,88)
Zn	0,67*	(0,21 - 0,88)	0,62*	(0,56 - 0,78)	0,65*	(0,45 - 0,88)	0,65*	(0,38 - 0,82)
Personal		**Helsinki**		**Utrecht**		**Barcelona**		**Pooled**
Component	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)	Median	(Q1 - Q3)
$PM_{2.5}$	0.60*	(0.19 - 0.78)	0.44*	(0.03 - 0.51)	0.64*	(0.13 - 1.03)	0.48*	(0.19 - 0.77)
Soot	0.42*	(0.17 - 0.61)	0.66*	(0.42 - 0.84)	0.40*	(0.31 - 0.91)	0.47*	(0.32 - 0.73)
NO_2	0.35*	(0.17 - 0.59)	0.37*	(0.26 - 0.58)	0.25*	(0.09 - 0.36)	0.31*	(0.14 - 0.56)
Cu	-0,93	(-2,25 - -0,31)	0,32	(-0,30 - 0,70)	0,61*	(0,04 - 1,62)	0,04*	(-0,43 - 0,87)
Fe	0,29*	(-0,06 - 0,74)	0,40*	(0,21 - 0,60)	0,80’	(0,13 - 2,41)	0,40*	(0,13 - 0,81)
K	0,36*	(0,17 - 0,69)	0,76*	(0,55 - 1,05)	0,73*	(0,49 - 1,58)	0,69*	(0,35 - 1,08)
Ni	0,47*	(0,23 - 0,65)	0,66*	(0,42 - 0,89)	0,72*	(0,57 - 1,13)	0,63*	(0,36 - 0,77)
S	0,67*	(0,44 - 0,79)	0,77*	(0,55 - 1,05)	0,87*	(0,55 - 1,10)	0,74*	(0,55 - 0,97)
Si	0,33*	(0,13 - 0,55)	0,65’	(0,19 - 0,82)	0,40	(-0,67 - 1,85)	0,39*	(-0,16 - 0,75)
V	0,69*	(0,44 - 0,85)	0,76*	(0,47 - 0,80)	0,64*	(0,50 - 1,14)	0,70*	(0,50 - 0,83)
Zn	0,38	(0,30 - 0,69)	0,66*	(0,51 - 0,95)	0,53*	(0,27 - 0,90)	0,55*	(0,34 - 0,75)

N=15 per city and n=45 for the pooled analysis * significant at the p<0.05 level ‘ significant at the p<0.10 level

Table 7 Regression analyses of the concentrations at the central site versus the indoor/personal concentrations, excluding measurements with Ratios>1.5. Median is the median Pearson's R of the analysis, Q1 the first quartile, Q3 the third quartile and n is the number of participants (with >2 measurements) included.

Indoor		Helsinki			Utrecht			Barcelona	
Component	Median	(Q1 - Q3)	n	Median	(Q1 - Q3)	n	Median	(Q1 - Q3)	n
$PM_{2.5}$	0,73*	(-0,22 - 0,98)	15	0,72*	(0,09 - 0,91)	15	0,69*	(0,47 - 0,85)	13
Soot	0,73*	(0,38 - 0,93)	15	0,83*	(0,79 - 0,95)	15	0,67*	(0,48 - 0,87)	15
NO_2	0,75*	(-0,13 - 0,93)	15	0,50*	(-0,09 - 0,80)	15	0,25	(-0,52 - 0,73)	15
Cu	0,73'	(0,05 - 0,91)	9	0,65	(0,04 - 0,83)	9	0,74*	(-0,35 - 0,94)	15
Fe	0,79*	(0,49 - 0,90)	15	0,64*	(0,24 - 0,91)	15	0,39*	(0,09 - 0,76)	9
K	0,83*	(0,66 - 0,91)	15	0,83*	(0,47 - 0,96)	11	0,64*	(0,10 - 0,82)	10
Ni	0,71*	(0,16 - 0,93)	15	0,93*	(0,87 - 0,97)	14	0,66*	(0,14 - 0,86)	14
S	0,88*	(0,80 - 0,97)	15	0,85*	(0,70 - 0,98)	15	0,84*	(0,74 - 0,89)	10
Si	0,93*	(0,78 - 0,99)	15	0,60*	(0,10 - 0,86)	13	0,40*	(0,18 - 0,77)	6
V	0,94*	(0,73 - 0,99)	15	0,91*	(0,72 - 0,98)	15	0,74*	(0,12 - 0,93)	10
Zn	0,89*	(0,57 - 0,94)	15	0,89*	(0,74 - 0,94)	15	0,67*	(0,24 - 0,85)	15
Personal		**Helsinki**			**Utrecht**			**Barcelona**	
Component	**Median**	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**
$PM_{2.5}$	0.70*	(0.15 - 0.92)	15	0.68*	(0.15 - 0.88)	15	0.28*	(0.06 - 0.68)	13
Soot	0.79*	(0.31 - 0.91)	15	0.87*	(0.71 - 0.95)	15	0.56*	(0.12 - 0.79)	15
NO_2	0.80*	(0.41 - 0.94)	15	0.73*	(0.61 - 0.89)	15	0.38*	(-0.13 - 0.79)	15
Cu	0.54*	(0.10 - 0.85)	8	0.79*	(0.23 - 0.92)	11	0.56	(-0.32 - 0.93)	14
Fe	0.50*	(0.38 - 0.83)	15	0.79*	(0.38 - 0.9)	15	0.41	(-0.38 - 0.86)	11
K	0.79*	(0.54 - 0.96)	15	0.84*	(-0.11 - 0.93)	12	0.58*	(0.39 - 0.94)	12
Ni	0.69*	(0.21 - 0.91)	15	0.89*	(0.70 - 0.95)	15	0.75*	(0.00 - 0.88)	15
S	0.93*	(0.87 - 0.98)	15	0.90*	(0.43 - 0.98)	15	0.85*	(0.67 - 0.96)	11
Si	0.87*	(0.70 - 0.98)	13	0.59*	(0.27 - 0.93)	12	-0.07	(-0.65 - 0.74)	8
V	0.91*	(0.74 - 0.97)	15	0.90*	(0.66 - 0.98)	15	0.87*	(0.33 - 0.94)	11
Zn	0.82*	(0.59 - 0.96)	15	0.81*	(0.41 - 0.91)	15	0.65*	(0.28 - 0.85)	15

*significant at the $p<0.05$ level ' significant at the $p<0.10$ level

for Fe these correlations were 0.80 for the child and 0.81 for the elderly pattern pooled across cities.

Home outdoor versus indoor/personal

The median correlation coefficients of the home outdoor concentrations with the personal/indoor concentrations are displayed in Table 5. Overall, the outdoor concentrations for the elements agreed well with the indoor and personal concentrations. The outdoor Cu concentrations did not correlate with the indoor and personal Cu concentrations in Helsinki, while a moderate to low correlation was observed in Utrecht and Barcelona. The outdoor Fe concentrations were moderately correlated with the indoor Fe concentrations in Barcelona and to the personal Fe concentrations in Helsinki. The personal Si concentrations were also less well correlated with the outdoor Si concentrations in all three cities. The correlations for most of the eight elements were higher than for total $PM_{2.5}$.

The indoor–outdoor regression slopes for S and V, were higher than for Cu and Fe (Table 6). Low regression slopes were also found for NO_2 in the three cities. The indoor and personal copper (Cu) slope in Helsinki were not statistically significant.

Discussion

Correlations with elemental exposure

Central site concentrations correlated well with home *outdoor* concentrations. Correlations were higher for S and V than for Cu, Fe and Si. The latter elements reflect the tail of coarse particles, which have more local sources compared to fine particles and therefore show different temporal patterns at different sites (close/far away from source).

A statistically significant temporal relationship of the concentrations at a central site with *personal* concentrations was found for most of the eight elements that were studied (Cu, Zn, Fe, K, Ni, V, Si and S). Correlations were stronger for S and V than for other elements. The weakest association was found for Cu.

The current findings are consistent with a previous study evaluating correlations in time between elemental personal and outdoor concentrations.[6] In the study by Janssen et al. the highest median temporal correlation coefficients for concentrations at a central monitoring site versus personal concentrations was found for sulfur (0.96 in Amsterdam and 0.90 in Helsinki). Likewise, high correlations were found for personal sulfur in our study. The associations for S and V were higher than for $PM_{2.5}$ in the three cities. For the personal measurements most time was spent at

home, therefore indoor sources have influence on the personal exposure. No indoor sources are of influence on the personal sulfur concentrations, which might explain these higher correlations. Furthermore, S is predominantly found in the submicrometer fraction of $PM_{2.5}$ which has been shown to have a higher infiltration rate.[21] Soot concentrations at the central site were not better correlated to the personal concentrations than the $PM_{2.5}$ concentrations (except in Barcelona), but the home outdoor soot concentrations were (Table 4, Table 5). Soot has relatively few indoor sources in non-smoking homes and a high infiltration factor and was thus expected to show larger correlations, as found in the previous study in Amsterdam and Helsinki where median correlations were higher than 0.90. Overall, the outdoor-indoor slope for soot was indeed higher than for $PM_{2.5}$ (Table 6). One difference between this study and the study by Janssen et al. is an overrepresentation of traffic sites. This was done to obtain sufficient contrast in component concentrations. An analysis stratified by site type, showed that central site personal exposure correlations were only moderately higher for background homes than for traffic homes. An important consequence is that the central site is useful for representing temporal variation for subjects living at both background and major road locations. Another difference is that 96 hour averages were used, as opposed to 24 hour averages in the study by Janssen at al. This may have contributed to the lower ranges in concentration in our study compared to the Janssen study and thus lower correlations. On the other hand, peak exposure due to indoor sources may have had reduced influence in our study because of the longer sample period. This might have increased the correlation of the ambient concentrations with the indoor and personal concentrations. In time series studies 24- or 48- hour averages are more usual. Another difference with the study by Janssen et al. is that the participants were elderly people, whereas our participants followed an elderly time activity pattern or a children's time activity pattern. In the latter fewer hours were spent at home. This could be an explanation for our lower correlations, although the effect of 4 out of 96 hours spent elsewhere is probably minimal. A stratified analysis showed no difference in correlation between the child and elderly pattern in our study, but the number of observations per subject may have been too small to detect differences.

Similar or marginally larger correlations between the central site and the personal concentrations were found for Fe, K, Ni and Zn. In Janssen et al., lower correlations were found for K than for $PM_{2.5}$. Low correlations were found for the transition metal Cu and for Si (in Utrecht and Barcelona). These elements are found in the coarser part of $PM_{2.5}$ and have low infiltration factors. Cu was more increased indoors than Si, suggesting that indoor sources other than resuspension of soil dust were present. Particularly for Cu, indoor sources may have contributed to the low correlation, as indoor concentrations exceeded outdoor concentrations. Similarly, in the study by Molnar et al., higher indoor than outdoor Cu concentrations were

found at homes but not at schools.[22] Suggested Cu sources were cooking and frying and electrical appliances like vacuum cleaners and hair dryers. When the samples with indoor/outdoor ratios>1.5 (or >2) were excluded from the analyses, the median correlations for Cu increased (Table 7 and OLS 5 Table S5). We used observed I/O ratios to identify indoor sources, as it has been argued that for epidemiological time series studies, the most relevant correlation is between central site concentration and the personal/indoor exposure from outdoor origin.[20,23] Methods to apportion indoor elemental concentrations to outdoor and indoor origin were not available. Excluding observations clearly affected by indoor sources (I/O > 1.5 or 2), increased the correlation of central site personal exposure particularly for Cu. This correlation may be more relevant for time series studies than the correlation with total indoor concentrations. We cannot exclude some influence of indoor sources in the remaining observations.

Consistent with the findings in Janssen et al. the ambient Si concentrations were better correlated to the personal concentrations in Helsinki than in Utrecht and Barcelona. In Helsinki the Si association was similar as the association of $PM_{2.5}$. Probably the main source of indoor Si aerosols is the resuspension of soil particles, carried indoors by adhering to shoes.[24] In Helsinki, it is more common to not wear shoes indoors than in Utrecht or Barcelona. Therefore in Helsinki the indoor Si concentrations are more dependent on infiltration and less on resuspension. Furthermore, in Helsinki fewer homes were on the ground or on the first floor then in Utrecht.

The coefficient of variance (CV) values for the duplicate measurements were substantially higher than the corresponding values in the ESCAPE project.[9] In ESCAPE, CV values were below 10% for S, Cu and Fe. One of the differences between ESCAPE and VE^{3}SPA is that different equipment was employed for the measurements. In ESCAPE, $PM_{2.5}$ samples were taken with Harvard Impactors and in VE^{3}SPA BGI personal pump units were used. Furthermore, for the calculation of the CV values in the VE^{3}SPA project, indoor and personal samples were included. The sample volumes were similar for both studies (20 m^3 in VE^{3}SPA versus 25 m^3 in ESCAPE). The relatively high CV values were still moderate compared to the large temporal variation in measured concentrations. Differences in measurement precision across components likely contributed only moderately to differences in observed correlations. While CV values for Cu and S were similar (Table 2), the outdoor–personal correlation was much higher for S than for Cu in the three cities. In Barcelona the CV value for Si was especially high, this may have contributed to the low correlation coefficient for central site-personal concentrations that was found for Si concentrations in Barcelona.

Correlations of $PM_{2.5}$ and NO_2

The longitudinal correlations of the central site versus personal concentrations for total $PM_{2.5}$ in our study were close to the overall median correlation of 0.54 in a review of 18 studies.[5] Significant heterogeneity was found between the studies, consistent with differences found in our study between the three cities.

We found fairly high correlations between central site and personal exposure for NO_2 as well, especially in Utrecht and Helsinki. In Utrecht and Barcelona a large fraction of the subjects used gas for cooking, a significant indoor source of NO_2. Our findings are in contrast with findings from a study in the US reporting very weak correlations between ambient and personal exposure.[25] A review of five studies reporting longitudinal correlations for eight populations of central site and personal NO_2 exposure reported an overall significant correlation of 0.16.[26] Significant heterogeneity was found between studies, with median correlation coefficients ranging from 0 to 0.6. Factors explaining this variability included age and pre-existing disease of the study population, presence of indoor sources, data quality (some studies included more than 50% of the observations below the detection limit) and sampling duration.[26] Our personal- central site slope of 0.3 was consistent with previous studies.[26]

Implications

There is currently substantial scientific interest in which components of particulate matter drive the observed health effects. There is little literature on short-term studies of daily variations of elemental concentrations and hospital admissions and mortality. Although there is considerable evidence that short-term variation in outdoor air pollution, measured as PM_{10}, $PM_{2.5}$ and soot, is well-correlated with variation in personal exposure,[5,27] the evidence for components is scarce. The high temporal correlations seen in the current study, between measured outdoor and indoor or personal exposure (Table 5), provides additional support for the use of outdoor measurements to characterize personal exposure in time series studies. We further found that central site concentrations were temporally highly correlated with the outdoor measurements made at the 15 homes dispersed over the cities (Table 4). This agrees with the previous findings by Janssen et al.[6] and endorses the application of a central measuring site in epidemiological time-series studies.

Overall, the temporal variation in the outdoor concentration of $PM_{2.5}$ components had a good association with the measured indoor and personal concentrations in all three cities. S and V, elements predominantly found in the fine fraction, showed the highest correlations. In conclusion, this study indicates that temporal variations in ambient concentrations at the home address and at central monitoring sites are reasonable proxies for

temporal variations in personal exposure to most of the elements we investigated.

References

1. Stanek, L.W.; Sacks, J.D.; Dutton, S.J.; Dubois, J.J.B. Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results. Atmos. Environ. 2011, 45, 5655-5663.

2. Kelly, F.J. and Fussell, J.C. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. 2012, 60, 504-526.

3. Rohr, A.C. and Wyzga, R.E. Attributing health effects to individual particulate matter constituents. Atmos. Environ. 2012, 62, 130-152.

4. Bell, M.L. Assessment of the health impacts of particulate matter characteristics. Res. Rep. Health Eff. Inst. 2012, 5-38.

5. Avery, C.L.; Mills, K.T.; Williams, R., et al Estimating error in using ambient PM2.5 concentrations as proxies for personal exposures: A review. Epidemiology 2010, 21, 215-223.

6. Janssen, N.A.H.; Lanki, T.; Hoek, G., et al Associations between ambient, personal, and indoor exposure to fine particulate matter constituents in Dutch and Finnish panels of cardiovascular patients. Occup. Environ. Med. 2005, 62, 868-877.

7. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Agreement of land use regression models with personal exposure measurements of particulate matter and nitrogen oxides air pollution. Environ. Sci. Technol. 2013, 47, 8523-8531.

8. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. Environ. Sci. Technol. 2012, 46, 11195-11205.

9. De Hoogh, K.; Wang, M.; Adam, M., et al Development of land use regression models for particle composition in twenty study areas in Europe. Environ. Sci. Technol. 2013, 47, 5778-5786.

10. Hjortenkrans, D.S.; Bergback, B.G.; Haggerud, A.V. Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. Environ. Sci. Technol. 2007, 41, 5224-5230.

11. Gietl, J.K.; Lawrence, R.; Thorpe, A.J.; Harrison, R.M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. Atmos. Environ. 2010, 44, 141-146.

12. Pio, C.A.; Legrand, M.; Alves, C.A., et al Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. Atmos. Environ. 2008, 42, 7530-7543.

13. Viana, M.; Kuhlbusch, T.A.J.; Querol, X., et al Source apportionment of particulate matter in Europe: A review of methods and results. J. Aerosol Sci. 2008, 39, 827-849.

14. Johansson, C.; Norman, M.; Burman, L. Road traffic emission factors for heavy metals.

Atmos. Environ. 2009, 43, 4681-4688.

15. Van Roosbroeck, S.; Jacobs, J.; Janssen, N.A.H.; Oldenwening, M.; Hoek, G.; Brunekreef, B. Long-term personal exposure to PM2.5, soot and NOx in children attending schools located near busy roads, a validation study. Atmos. Environ. 2007, 41, 3381-3394.

16. Cyrys, J.; Eeftens, M.; Heinrich, J., et al Variation of NO2 and NOx concentrations between and within 36 European study areas: Results from the ESCAPE study. Atmos. Environ. 2012, 62, 374-390.

17. Janssen, N.A.H.; Hoek, G.; Brunekreef, B.; Harssema, H.; Mensink, I.; Zuidhof, A. Personal sampling of particles in adults: Relation among personal, indoor, and outdoor air concentrations. Am. J. Epidemiol. 1998, 147, 537-547.

18. Janssen, N.A.H.; De Hartog, J.J.; Hoek, G., et al Personal exposure to fine particulate matter in elderly subjects: Relation between personal, indoor, and outdoor concentrations. Journal of the Air and Waste Management Association 2000, 50, 1133-1143.

19. Hänninen, O.; Hoek, G.; Mallone, S., et al Seasonal patterns of outdoor PM infiltration into indoor environments: Review and meta-analysis of available studies from different climatological zones in Europe. Air Qual. Atmos. Health 2011, 4, 221-233.

20. Wilson, W.E. and Brauer, M. Estimation of ambient and non-ambient components of particulate matter exposure from a personal monitoring panel study. J. Expos. Sci. Environ. Epidemiol. 2006, 16, 264-274.

21. Long, C.M. and Sarnat, J.A. Indoor-outdoor relationships and infiltration behavior of elemental components of outdoor PM2.5 for Boston-area homes. Aerosol. Sci. Technol. 2004, 38, 91-104.

22. Molnar, P.; Bellander, T.; Sallsten, G.; Boman, J. Indoor and outdoor concentrations of PM2.5 trace elements at homes, preschools and schools in Stockholm, Sweden. J. Environ. Monit. 2007, 9, 348-357.

23. Sheppard, L. Acute air pollution effects: consequences of exposure distribution and measurements. J. Toxicol. Environ. Health Part A 2005, 68, 1127-1135.

24. Diemel, J.A.; Brunekreef, B.; Boleij, J.S.; Biersteker, K.; Veenstra, S.J. The Arnhem Lead Study. II. Indoor pollution, and indoor/outdoor relationships. Environ. Res. 1981, 25, 449-456.

25. Sarnat, J.A.; Koutrakis, P.; Suh, H.H. Assessing the Relationship between Personal Particulate and Gaseous Exposures of Senior Citizens Living in Baltimore, MD. J. Air Waste Manage. Assoc. 2000, 50, 1184-1198.

26. Meng, Q.Y.; Svendsgaard, D.; Kotchmar, D.J.; Pinto, J.P. Associations between personal exposures and ambient concentrations of nitrogen dioxide: A quantitative research synthesis. Atmos. Environ. 2012, 57, 322-329.

27. Brunekreef, B.; Janssen, N.A.; de Hartog, J.J., et al Personal, indoor, and outdoor exposures to PM2.5 and its components for groups of cardiovascular patients in Amsterdam and Helsinki. Res. Rep. Health Eff. Inst. 2005, 1-70; discussion 71-79.

Supplemental Information

CV equation and concentration calculations

$$CV = \frac{\sqrt{\frac{\sum_{i=1}^{n}(S_i - D_i)^2}{2*n}}}{\frac{\sum_{i=1}^{n}(S_i + D_i)}{2*n}} * 100\% \quad (1)$$

Equation (1): Calculation of the coefficient of variation. Where n is the number of duplicates and i is the sampling round (1 to n). S is the concentration of sample i and D is the concentration of corresponding duplicate i.[1]

The concentrations, in ng/m^3, were calculated using the analyzed concentration minus the city-specific mean blank concentration divided by the sampled volume and multiplied by the exposed filter area.

$$CC_i = 7.8*(C_i\text{-}MBL)/V_s *1000 \quad (2)$$

Equation (2): calculation of the concentrations. Where CC_i is the calculated concentration for the sample i (ng/m^3), 7.8 is the exposed filter area (cm^2), C_i is the analyzed concentration for sample i (µg/cm^2). MBL is the mean blank concentration (µg/cm^2) and V_s is the sampled volume in m^3

Imputation central site

In the Netherlands, measurements were done in 32 weeks (2 extra weeks were scheduled to replace some missing data). During two of these measuring weeks, $PM_{2.5}$ data from the central site were missing because of technical failure. In Spain, the number of measuring weeks was 30. Out of these 30 weeks, 7 had missing $PM_{2.5}$ data at the central site. Four missing measurements occurred because no units were available and three because of technical failure.

For the missing measurements on the central site in Spain and the Netherlands, imputation was applied. As there were no elemental concentrations measured in the networks, we had to rely on PM_{10}, $PM_{2.5}$ and NO_2/NO_x to impute elements. We only imputed if there was a high correlation in the available VE^{3}SPA measurements, as we preferred to have some missing data over poor data. The R squares had to be larger than 0,50 for the formula to be used for imputation. In Utrecht, only for

sulfur (S) the imputation formula met this criterion. In Barcelona, we could use the imputation formula for copper (Cu), nickel (Ni) and zinc (Zn). In Helsinki there were no missing data for the central site.

The measurements on the central site were compared to measurements at fixed monitoring sites from the RIVM ('Rijksinstituut voor Volksgezondheid en Milieu', the National institute for Public Health and the Environment) in the Netherlands and the National Network in Barcelona (Gencat, Generalitat de Catalunya). The regression formula comparing the VE^{3}SPA central site with the fixed site was used to calculate the concentrations for the missing data (Table S1).

Table S1 Imputation formula's for S in Utrecht and Cu, Ni and Zn in Barcelona

City	Element	Comp, site	N	Intercept	β	R^2
Utrecht	S	PM_{10}, 633	30	-170.28	36.21	0.66
Barcelona	Cu	NO_x, Hospitalet	23	-3.21	0.18	0.77
Barcelona	Ni	PM_{10}, Hebron	17	-2.50	0.20	0.57
Barcelona	Zn	NO_x, Hospitalet	23	-7.32	0.85	0.54

The imputed element and the independent component (comp) with the name of the fixed monitor site, the number of measurements in the linear regression (n), the intercept (α), the Beta (β) and the R2 are given and entered in the imputation formula.

Analyses without busy streets and with busy streets only

Table S2 The median of individual correlation coefficients (Pearson's R) of the measurements at the central site and the outdoor/indoor/personal measurements (of the participants with >2 measurements), without the busy street sites (no traffic) and with the busy street sites only (traffic).

Outdoor	Helsinki				Utrecht				Barcelona				Pooled			
	No traffic		Traffic		No traffic		Traffic		No traffic		Traffic		No traffic		Traffic	
Component	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n
$PM_{2.5}$	0.84*	10	0.97*	5	0.91*	10	0.95*	5	0.79*	10	0.79*	5	0.84*	30	0.93*	15
Soot	0.89*	10	0.90*	5	0.90*	10	0.87*	5	0.82*	10	0.60*	5	0.88*	30	0.81*	15
NO_2	0.96*	10	0.99*	5	0.95*	10	0.66*	5	0.87*	10	0.89	5	0.92*	30	0.87*	15
Cu	0.71*	10	0.78'	5	0.82*	10	0.49'	5	0.49*	10	0.25	5	0.62*	30	0.75*	15
Fe	0.80*	10	0.51*	5	0.74*	10	0.58'	5	0.51	9	0.99	3	0.77*	29	0.58*	13
K	0.94*	10	0.99*	5	0.88*	10	0.94*	5	0.71*	9	0.90	3	0.89*	29	0.97*	13
Ni	0.64*	10	0.91	5	0.81*	10	0.86*	5	0.62	10	0.63*	5	0.66*	30	0.83*	15
S	0.98*	10	0.94*	5	0.91*	10	0.90*	5	0.85*	9	0.93*	3	0.92*	29	0.93*	13
Si	0.92*	10	0.85*	5	0.62*	10	0.79*	5	0.26	9	0.71	3	0.76*	29	0.79*	13
V	0.94*	10	0.93*	5	0.96*	10	0.92*	5	0.68*	9	0.98*	3	0.92*	29	0.94*	13
Zn	0.92*	10	0.97*	5	0.94*	10	0.91*	5	0.67*	10	0.56*	5	0.90*	30	0.91*	15
Indoor	**Helsinki**				**Utrecht**				**Barcelona**				**Pooled**			
	No traffic		Traffic		No traffic		Traffic		No traffic		Traffic		No traffic		Traffic	
Component	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n	Median	n
$PM_{2.5}$	0.28	10	0.85*	5	0.44*	10	0.91	5	0.67*	10	0.51'	5	0.53*	30	0.74*	15
Soot	0.74*	10	0.80*	5	0.84*	10	0.74*	5	0.52*	10	0.71*	5	0.79*	30	0.74*	15
NO_2	0.31	10	0.56	5	0.50*	10	0.53	5	0.35	10	0.41	5	0.47*	30	0.46'	15
Cu	0.00	10	-0.54	5	0.33'	10	0.20	5	0.62'	10	0.34'	5	0.39*	30	0.09	15

Table S2 continued

Fe	0.86*	10	0.74*	5	0.71*	10	0.64'	5	0.64*	9	-0.37	1	0.77*	29	0.64*	11
K	0.66*	10	0.27*	5	0.46'	10	0.93'	5	0.64*	9	-0.06	1	0.64*	29	0.76*	11
Ni	0.68	10	0.83	5	0.88'	10	0.88*	5	0.66	10	0.72'	5	0.75*	30	0.83*	15
S	0.86*	10	0.95*	5	0.82*	10	0.91*	5	0.76*	9	0.96	1	0.83*	29	0.95*	11
Si	0.82*	10	0.80*	5	0.25*	10	0.82'	5	0.62	9	0.04	1	0.62*	29	0.80*	11
V	0.87*	10	0.94*	5	0.91*	10	0.97*	5	0.62*	9	0.88	1	0.90*	29	0.94*	11
Zn	0.78*	10	0.94*	5	0.84*	10	0.87*	5	0.60*	10	0.71*	5	0.75*	30	0.89*	15
Personal	**Helsinki**				**Utrecht**				**Barcelona**				**Pooled**			
	No traffic		**Traffic**		**No traffic**		**Traffic**		**No traffic**		**Traffic**		**No traffic**		**Traffic**	
Component	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**
$PM_{2.5}$	0.19	10	0.81*	5	0.69*	10	0.66*	5	0.46'	9	0.28'	5	0.57*	29	0.57*	15
Soot	0.71*	10	0.68*	5	0.86*	10	0.75*	5	0.63	10	0.56*	5	0.76*	30	0.71*	15
NO_2	0.76*	10	0.47'	5	0.73*	10	0.49	5	0.45*	10	0.46	5	0.72*	30	0.47*	15
Cu	0.10	10	-0.27	5	0.21	10	0.53*	5	0.70*	10	0.18	5	0.21*	30	0.18	15
Fe	0.48*	10	0.78'	5	0.76*	10	0.83*	5	0.25'	8	0.65	4	0.48*	28	0.76*	14
K	0.73*	10	0.64*	5	0.43'	10	0.78'	5	0.63*	8	0.74*	4	0.69*	28	0.71*	14
Ni	0.42	10	0.84*	5	0.85*	10	0.88*	5	0.62	10	0.68'	5	0.76*	30	0.82*	15
S	0.95*	10	0.92*	5	0.89*	10	0.90*	5	0.69'	8	0.96'	4	0.88*	28	0.94*	14
Si	0.71*	10	0.53*	5	0.47'	10	0.56'	5	-0.13	8	-0.40	4	0.37*	28	0.51'	14
V	0.92*	10	0.91*	5	0.92*	10	0.90*	5	0.65'	8	0.94*	4	0.91*	28	0.91*	14
Zn	0.82*	10	0.96*	5	0.87*	10	0.76*	5	0.83*	10	0.41'	5	0.83*	30	0.55*	15

*significant at the p<0.05 level ` significant at the p<0.10 level

Associations with outdoor NO_2 and $PM_{2.5}$

Table S3 The median of individual correlation coefficients (Pearson's R) of the associations of home outdoor NO_2 and $PM_{2.5}$ with the Cu, Zn, Fe, K, Ni, V, Si, and S outdoor/indoor/personal concentrations in Helsinki, Utrecht and Barcelona (N=15).

		NO_2			$PM_{2.5}$		
		Outdoor	Indoor	Personal	Outdoor	Indoor	Personal
Helsinki	Cu	0.42	0.44	0.42	0.51	0.59	0.22
	Zn	0.57	0.31	0.34	0.88	0.81	0.78
	Fe	0.52	0.61	0.58	0.77	0.58	0.34
	K	0.73	0.54	0.35	0.73	0.48	0.40
	Ni	0.30	0.27	0.41	0.78	0.49	0.48
	V	0.22	0.41	0.35	0.83	0.75	0.67
	Si	0.37	0.43	0.66	0.64	0.44	0.43
	S	0.43	0.54	0.61	0.91	0.86	0.75
Utrecht	Cu	0.65	0.71	0.70	0.37	0.76	0.77
	Zn	0.61	0.75	0.40	0.59	0.72	0.55
	Fe	0.63	0.61	0.47	0.45	0.48	0.37
	K	0.52	0.54	0.37	0.72	0.64	0.65
	Ni	0.39	0.27	0.43	0.49	0.50	0.49
	V	0.31	0.41	0.30	0.47	0.62	0.58
	Si	0.35	0.43	0.38	0.50	0.39	0.27
	S	0.50	0.54	0.36	0.77	0.73	0.60
Barcelona	Cu	0.71	0.75	0.67	0.78	0.66	0.50
	Zn	0.60	0.63	0.73	0.66	0.72	0.59
	Fe	0.63	0.60	0.67	0.64	0.60	0.48
	K	0.70	0.67	0.64	0.86	0.73	0.61
	Ni	0.54	0.55	0.35	0.62	0.52	0.40
	V	0.39	0.26	0.64	0.46	0.41	0.46
	Si	0.48	0.40	0.72	0.39	0.45	0.63
	S	0.40	0.37	0.43	0.36	0.33	0.27

Indoor/outdoor and personal/outdoor Ratios

The indoor/outdoor and personal/outdoor ratios were calculated for all measurements. Next, the median and quartiles were determined per city (Table S4). The median ratio's for Cu were higher than 1 for Cu in Helsinki and Utrecht, suggesting that indoor sources are important for this element. We also see some evidence for Si indoor sources in this table.

Table S4 The indoor/outdoor and personal/outdoor ratios. The median, the first and third quartile (Q1 – Q3) and the 5-95 percentile (p5-p95) ratios are shown.

Indoor/Outdoor		Helsinki			Utrecht			Barcelona	
	Median	(Q1 - Q3)	(p5 - p95)	Median	(Q1 - Q3)	(p5 - p95)	Median	(Q1 - Q3)	(p5 - p95)
$PM_{2.5}$	0.94	(0.68 - 1.18)	(0.29 - 2.68)	0.77	(0.59 - 0.99)	(0.4 - 1.36)	0.89	(0.71 - 1.15)	(0.58 - 1.93)
Soot	0.73	(0.56 - 0.84)	(0.39 - 1.38)	0.76	(0.69 - 0.85)	(0.56 - 1.09)	0.81	(0.71 - 0.93)	(0.57 - 1.18)
NO_2	0.61	(0.41 - 0.81)	(0.22 - 1.39)	0.68	(0.50 - 0.94)	(0.38 - 1.56)	0.76	(0.56 - 0.93)	(0.37 - 1.23)
Cu	2.18	(0.90 - 5.88)	(0.34 - 12.66)	1.25	(0.79 - 1.84)	(0.54 - 4.13)	0.89	(0.69 - 1.43)	(0.45 - 2.53)
Fe	0.55	(0.36 - 0.70)	(0.23 - 0.97)	0.68	(0.54 - 0.84)	(0.33 - 1.03)	0.67	(0.54 - 0.93)	(0.37 - 1.83)
K	0.88	(0.70 - 1.14)	(0.39 - 3.39)	1.07	(0.89 - 1.46)	(0.68 - 3.8)	0.90	(0.76 - 1.09)	(0.58 - 1.51)
Ni	0.57	(0.29 - 0.93)	(-0.81 - 1.31)	0.81	(0.49 - 1.04)	(-0.28 - 2.05)	0.79	(0.60 - 1.04)	(0.21 - 1.40)
S	0.65	(0.46 - 0.82)	(0.32 - 0.98)	0.77	(0.71 - 0.87)	(0.61 - 1.09)	0.79	(0.68 - 0.98)	(0.53 - 1.44)
Si	0.89	(0.63 - 1.26)	(0.28 - 2.98)	1.17	(0.87 - 1.68)	(0.65 - 4.65)	1.05	(0.78 - 1.92)	(0.53 - 4.28)
V	0.59	(0.33 - 0.82)	(-0.05 - 1.19)	0.77	(0.58 - 0.95)	(0.35 - 1.81)	0.77	(0.64 - 0.95)	(0.44 - 1.46)
Zn	0.52	(0.35 - 0.78)	(0.21 - 1.07)	0.79	(0.7 - 0.92)	(0.52 - 1.24)	0.74	(0.63 - 1.01)	(0.50 - 1.31)
Personal/Outdoor		**Helsinki**			**Utrecht**			**Barcelona**	
	Median	**(Q1 - Q3)**	**(p5 - p95)**	**Median**	**(Q1 - Q3)**	**(p5 - p95)**	**Median**	**(Q1 - Q3)**	**(p5 - p95)**
$PM_{2.5}$	0.91	(0.66 - 1.19)	(0.38 - 1.97)	0.71	(0.58 - 0.95)	(0.33 - 1.5)	1.13	(0.82 - 1.98)	(0.48 - 3.76)
Soot	0.72	(0.62 - 0.90)	(0.42 - 1.32)	0.80	(0.68 - 0.94)	(0.49 - 1.27)	0.82	(0.68 - 1.07)	(0.42 - 1.35)
NO_2	0.67	(0.54 - 0.89)	(0.39 - 1.23)	0.71	(0.57 - 0.91)	(0.37 - 1.36)	0.70	(0.60 - 0.89)	(0.44 - 1.24)
Cu	2.35	(1.22 - 5.60)	(0.42 - 14.36)	1.09	(0.75 - 1.54)	(0.48 - 4.33)	1.08	(0.76 - 1.85)	(0.44 - 4.32)
Fe	0.87	(0.61 - 1.24)	(0.28 - 2.33)	0.72	(0.57 - 0.90)	(0.32 - 1.42)	1.07	(0.70 - 2.27)	(0.33 - 11.37)
K	0.95	(0.74 - 1.42)	(0.45 - 2.24)	1.07	(0.91 - 1.37)	(0.6 - 2.84)	1.08	(0.82 - 1.77)	(0.50 - 4.83)
Ni	0.56	(0.32 - 0.82)	(-0.29 - 1.81)	0.78	(0.54 - 1.21)	(-0.78 - 6.30)	0.85	(0.59 - 1.27)	(0.11 - 2.87)
S	0.62	(0.47 - 0.75)	(0.36 - 0.96)	0.76	(0.68 - 0.87)	(0.48 - 1.48)	0.84	(0.66 - 1.09)	(0.35 - 1.88)
Si	1.07	(0.66 - 1.81)	(0.36 - 3.86)	1.37	(0.92 - 2.13)	(0.56 - 5)	2.24	(1.14 - 5.8)	(0.56 - 17.21)
V	0.59	(0.37 - 0.80)	(0.12 - 1.18)	0.74	(0.57 - 0.93)	(0.36 - 1.53)	0.82	(0.62 - 1.13)	(0.23 - 1.92)
Zn	0.59	(0.41 - 0.83)	(0.26 - 1.59)	0.80	(0.66 - 0.97)	(0.5 - 1.71)	0.82	(0.59 - 1.15)	(0.34 - 2.60)

In additional analyses, the indoor and personal measurements that had an indoor/outdoor ratio>2 or ratio>1.5 were excluded from the linear regression, to reduce the influence from indoor sources. Again, participants were only included in the analyses if they had more than 2 measurements (Table S5 and Table S6).

Table S5 Regression analyses of the concentrations at the central site versus the indoor/personal concentrations, excluding measurements with Ratios>2. Median is the median Pearson's R of the analysis, Q1 the first quartile, Q3 the third quartile and n is the number of participants (with >2 measurements) included.

Component		**Helsinki**			**Indoor Utrecht**			**Barcelona**	
	Median	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**
$PM_{2.5}$	0,73*	(-0,17 - 0,85)	15	0,59*	(0,09 - 0,91)	15	0,74*	(0,51 - 0,89)	15
Soot	0,73*	(0,38 - 0,91)	15	0,83*	(0,79 - 0,95)	15	0,56*	(0,38 - 0,87)	15
NO_2	0,73*	(-0,13 - 0,92)	15	0,51*	(0,38 - 0,77)	15	0,25	(-0,52 - 0,73)	15
Cu	0,32	(-0,11 - 0,87)	9	0,47	(-0,08 - 0,84)	14	0,76*	(0,08 - 0,94)	15
Fe	0,79*	(0,49 - 0,90)	15	0,64*	(0,24 - 0,87)	15	0,57*	(0,09 - 0,77)	10
K	0,83*	(0,49 - 0,92)	15	0,85*	(0,46 - 0,95)	12	0,64*	(0,10 - 0,83)	10
Ni	0,71*	(0,16 - 0,93)	15	0,88*	(0,70 - 0,94)	15	0,72*	(0,14 - 0,86)	15
S	0,88*	(0,80 - 0,97)	15	0,85*	(0,70 - 0,98)	15	0,84*	(0,74 - 0,89)	10
Si	0,84*	(0,68 - 0,99)	15	0,62*	(0,10 - 0,86)	13	0,71*	(0,19 - 0,77)	7
V	0,94*	(0,73 - 0,99)	15	0,91*	(0,72 - 0,97)	15	0,74*	(0,12 - 0,93)	10
Zn	0,89*	(0,57 - 0,94)	15	0,89*	(0,74 - 0,94)	15	0,67*	(0,21 - 0,85)	15
Component		**Helsinki**			**Personal Utrecht**			**Barcelona**	
	Median	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**	**Median**	**(Q1 - Q3)**	**n**
$PM_{2.5}$	0.70*	(0.13 - 0.90)	15	0.68*	(0.15 - 0.88)	15	0.40*	(0.09 - 0.72)	14
Soot	0.79*	(0.31 - 0.93)	15	0.87*	(0.71 - 0.95)	15	0.62*	(0.12 - 0.79)	15
NO_2	0.72*	(0.41 - 0.94)	15	0.73*	(0.60 - 0.90)	15	0.38*	(-0.13 - 0.79)	15
Cu	0.38	(-0.09 - 0.79)	9	0.49	(-0.46 - 0.80)	14	0.60*	(-0.28 - 0.85)	14
Fe	0.50*	(0.33 - 0.83)	15	0.79*	(0.12 - 0.90)	15	0.51'	(0.06 - 0.76)	12
K	0.76*	(0.54 - 0.96)	15	0.78*	(0.16 - 0.90)	13	0.58*	(0.39 - 0.94)	12
Ni	0.69*	(0.15 - 0.91)	15	0.88*	(0.70 - 0.94)	15	0.68*	(0.00 - 0.86)	15
S	0.93*	(0.87 - 0.98)	15	0.90*	(0.43 - 0.98)	15	0.90*	(0.69 - 0.96)	12
Si	0.81*	(0.52 - 0.91)	14	0.63*	(0.41 - 0.93)	13	-0.28	(-0.51 - 0.70)	9
V	0.91*	(0.74 - 0.97)	15	0.90*	(0.66 - 0.98)	15	0.88*	(0.44 - 0.96)	12
Zn	0.82*	(0.59 - 0.96)	15	0.80*	(0.39 - 0.91)	15	0.65*	(0.28 - 0.85)	15

*significant at the p<0.05 level ' significant at the p<0.10 level

Influence of time activity patterns on correlation between central site and personal exposure

Table S6 Median of individual Pearson correlation coefficients of central site and personal exposure stratified by time activity pattern (child or elderly)

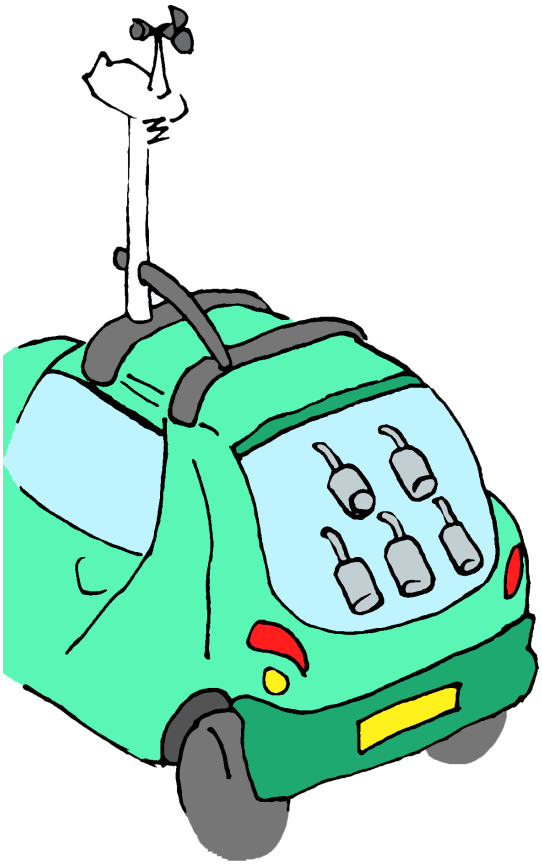
		Helsinki		Utrecht		Barcelona		Pooled	
Component	**Pattern**	**Median**	**n**	**Median**	**n**	**Median**	**n**	**Median**	**n**
$PM_{2.5}$	Child	0.90	12	0.81	12	0.62	8	0.81	32
	Elderly	0.17	11	0.99	10	0.04	9	0.32	30
Soot	Child	0.84	12	0.95	12	0.74	10	0.91	34
	Elderly	0.83	11	0.91	10	0.64	9	0.82	30
NO_2	Child	0.79	15	0.72	13	0.48	13	0.72	41
	Elderly	0.76	14	0.80	12	0.38	13	0.74	39
Cu	Child	0.06	12	0.52	9	0.43	10	0.35	31
	Elderly	-0.10	11	0.04	10	0.54	9	0.29	30
Fe	Child	0.86	12	0.93	9	0.60	4	0.80	25
	Elderly	0.59	11	0.97	10	-0.46	5	0.81	26
K	Child	0.73	12	0.58	9	0.88	4	0.69	25
	Elderly	0.56	11	0.60	10	0.58	5	0.57	26
Ni	Child	0.78	12	0.91	9	0.55	10	0.79	31
	Elderly	0.96	11	0.98	10	0.40	6	0.94	27
S	Child	0.98	12	0.91	12	-0.03	4	0.93	28
	Elderly	0.95	11	1.00	10	0.79	5	0.97	26
Si	Child	0.69	12	-0.12	9	-0.66	4	0.27	25
	Elderly	0.94	11	0.73	10	0.04	5	0.62	26
V	Child	0.97	12	0.94	9	0.29	4	0.94	25
	Elderly	0.96	11	1.00	10	0.72	5	0.96	26
Zn	Child	0.62	12	0.82	9	0.71	10	0.64	31
	Elderly	0.87	11	0.99	10	0.80	9	0.95	30

Table S7 Median of individual Pearson correlation coefficients of central site and personal exposure for subjects stratified by time spent at home (below or above city-specific median)

Component	Time Home	Helsinki	Utrecht	Barcelona	Pooled
Cu	< median	-0.05	0.60	0.63	0.31
	> median	0.17	0.19	-0.13	0.17
Fe	< median	0.79	0.81	0.34	0.75
	> median	0.46	0.74	0.08	0.49
K	< median	0.51	0.47	0.78	0.70
	> median	0.70	0.70	0.46	0.68
Ni	< median	0.78	0.89	0.07	0.72
	> median	0.17	0.81	0.82	0.81
S	< median	0.93	0.87	0.78	0.90
	> median	0.93	0.95	0.97	0.95
Si	< median	0.60	0.09	-0.07	0.33
	> median	0.70	0.63	0.24	0.56
V	< median	0.94	0.82	0.91	0.90
	> median	0.91	0.95	0.90	0.93
Zn	< median	0.85	0.58	0.76	0.80
	> median	0.71	0.85	0.41	0.80

References

1. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric Environment* **2012,** *62,* 303-317.



Chapter 5

Spatial variation of ultrafine particles and black carbon in two cities: results from a short-term measurement campaign

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Abstract

Recently, short-term monitoring campaigns have been carried out to investigate the spatial variation of air pollutants within cities. Typically, such campaigns are based on short-term measurements at relatively large numbers of locations. It is largely unknown how well these studies capture the spatial variation of long term average concentrations. The aim of this study was to evaluate the within-site temporal and between-site spatial variation of the concentration of ultrafine particles (UFP) and black carbon (BC) in a short-term monitoring campaign.

In Amsterdam and Rotterdam (the Netherlands) measurements of number counts of particles larger than 10 nanometer as a surrogate for UFP and BC were performed at 80 sites per city. Each site was measured in three different seasons of 2013 (winter, spring, summer). Sites were selected from busy urban streets, urban background, regional background and near highways, waterways and green areas, to obtain sufficient spatial contrast. Continuous measurements were performed for 30 minutes per site between 9 and 16 hr to avoid traffic spikes of the rush hour. Concentrations were simultaneously measured at a reference site to correct for temporal variation. We calculated within- and between-site variance components reflecting temporal and spatial variation. Variance ratios were compared with previous campaigns with longer sampling durations per sample (24 hour to 14 days).

The within-sites variance was 2.17 and 2.44 times higher than the between-sites variance for UFP and BC, respectively. In two previous studies based upon longer sampling duration much smaller variance ratios were found (0.31 and 0.09 for UFP and BC). Correction for temporal variation from a reference site was less effective for the short-term monitoring campaign compared to the campaigns with longer duration. Concentrations of BC and UFP were on average 1.6 and 1.5 times higher at urban street compared to urban background sites. No significant differences between the other site types and urban background were found.

The high within to between-site concentration variance may result in loss of precision and low explained variance when average concentrations from short-term campaigns are used to develop land use regression models.

Introduction

Risk assessment of morbidity and mortality associated with traffic-related air pollution exposure is a difficult challenge.[1] Monitoring networks of air quality can provide appropriate information on temporal variability of pollutant concentrations, however small-scale spatial variation is typically not well-characterized by these networks.[2] Ultrafine particles are airborne nanoparticles with a diameter less than 100 nm. They typically account for approximately 80% of the total particle number concentration but contribute little to ambient particle mass.[3] Ultrafine particles have high spatial and temporal variability within a city.[4] Close to highways the concentration of ultrafine particles can be up to 25 times higher than at background sites.[5] Ultrafine particle (UFP) concentrations can drop to background levels in open terrain approximately 300 meters from a source. Because of especially dispersion processes, the total particle number concentration decreases rapidly with increasing distance from the source. UFP has a higher spatial variation than for example $PM_{2.5}$ which is characterized by a high regional background.[5] Because of the shorter atmospheric lifetime of ultrafine particles (related to processes including coagulation, volatilization and deposition) the regional background is less important than for fine particles.

Thus far, there are very few epidemiology studies on health effects of long-term UFP exposure, partly due to the lack of spatially resolved exposure data.[1] UFP is typically not measured in routine monitoring networks. The instruments available to measure ultrafine particle or total particle number concentrations, are either too expensive or require too much operator interference to be used in the monitoring campaigns designed to build land use regression models.[6] These campaigns typically involve selection of 40 – 80 sampling sites in a study area and monitoring of 1 to 2 weeks per site with instruments left unattended.[6,7] As an alternative, in the last few years several short-term or mobile measuring campaigns have been carried out with constant technician supervision to measure the spatial variation of UFP and other pollutants in cities.[2,8-14] The campaigns were often designed to develop land use regression models and typically have short sampling periods per location (15-60 minutes) and a small number of repeats at each site. On-road mobile monitoring has also been used with typically even shorter sampling periods in a specific street but more repeats.[2,9,11-14] The strength of the design is the large number of sites that can be measured, e.g. over 600 sites in the Girona study.[11] Because of the short sampling period temporal fluctuations have more impact on results of measurements than in studies using longer sampling times. Therefore, these short-term sampling campaigns might be less precise in determining spatial variation of long-term average concentrations, which could affect the development of robust land use regression models based upon the monitored average concentrations. Short-term campaigns are characterized by monitoring at different sites and different times. A major

challenge of short-term campaigns is therefore to separate temporal variation from spatial variation, often achieved by a one or a few continuous monitoring sites. Little attention has been paid to methodological issues of short-term campaigns, including the separation of spatial (between-site) and temporal variation (within-site) and the effectiveness of correction for temporal variation to account for non-simultaneous measurements at different sites.

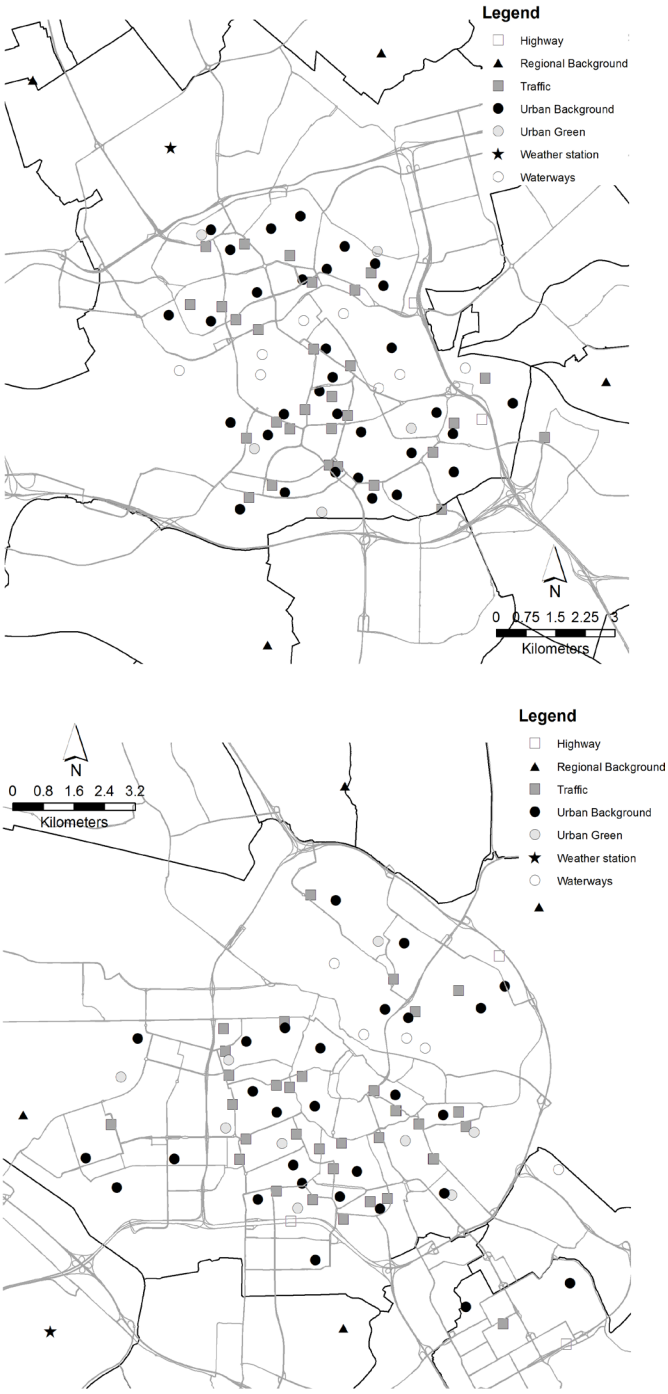
The Measurements of Ultrafine particles and Soot in Cities (MUSiC) study focused on the improvement of exposure assessment of ultrafine particles (UFP) and black carbon (BC) using a short-term monitoring campaign. Ambient concentrations of UFP and BC were measured at 161 locations for 30 minutes, three times at each site, in different seasons. The aim of this paper is to evaluate the between and within-site variance of the short-term air pollution measurements reflecting spatial and temporal variability. The estimated between and within-site variance components were compared with previous monitoring campaigns with longer term measurements of BC and UFP. The effectiveness of correcting for temporal variation using a single continuous reference site was explored.

Materials & methods

Study design

We selected 80 sites in Rotterdam and 81 in Amsterdam. Six different types of sites were defined: street, urban background, urban green, waterway, highway and regional background sites. For site selection, the ESCAPE protocol was followed.[7] Street sites were located in major roads defined as a traffic intensity of more than 10,000 vehicles per day. Urban background sites were sites with no major road within a distance of 100 m. Urban green sites were background sites at the edge of a park. Waterway sites were sites selected on the edge of a water body with potentially significant shipping emissions. Highways sites were sites within 100 m of a road classified as a highway. Regional background sites were background sites selected typically about 10 km outside the city. All sites were selected to minimize influences of other local sources (e.g. gas stations) and were situated close to building facades, except for the water body sites. In both cities approximately 30 street sites and 30 urban background sites were selected. Street sites were overrepresented to increase the contrast in concentrations. Furthermore four regional background sites, roughly at every cardinal direction outside the city, were chosen. Further details about the sites can be found in the supplemental information (SI, Table S1 and S2). The average traffic intensity was about 13,000 vehicles per day for the street sites, 155,000 for the highway sites and less than 1,000 for the other sites (Table S1). The fraction of heavy duty vehicles

Figure 1 Study Areas, Rotterdam (top) and Amsterdam (bottom)



(using diesel) was 8% for the highway sites and 4% for the street sites. For the other sites counts were between 2 and 6% but these fractions are less reliable because of low counts. The distribution of sites in the two cities is shown in Figure 1. Examples of two sites are given in Figure S1. Highway sites were located between 22 and 79 meters from the edge of the highway, with vegetation, earth wall or noise barriers in between (Table S2).

The ambient concentrations of ultrafine particles and black carbon were measured in real-time for 30 minutes at each site. An electric car (REVA, Mahindra Reva Electric Vehicles Pvt. Ltd., Bangalore, India) was used to transport the equipment to the sites and as equipment support. The instruments were installed in the back of the car. Because of seasonal variations in air pollutant concentrations, measurements were conducted in winter (January-March), spring (April-May) and summer (June-July) 2013. In total 483 measurements at 161 sites were conducted, spread over six measurement campaigns (three seasons, two cities).

Equipment

A CPC 3007 (TSI Inc. Tennessee, USA) was installed in the back of the car to measure UFP. The CPC 3007 measures particles above 10 nm and includes particles larger than 1000 nm. Total particle number counts are typically dominated by ultrafine particles, defined as particles <100 nm.[3,4] This instrument had 1 second intervals between measurements. A Micro Aethalometer (Aethlabs, CA, USA) was used to measure BC continuously, with 1 minute intervals. The BC monitoring interval was set at 1 minute because of insufficient precision at shorter time intervals. The rear window of the car was replaced by PET (Polyethylene terephthalate) glass. Conductive silicone tubes (TSI Inc. Tennessee, USA) connected the instrument inlets to copper pipes, which were placed through holes in the PET glass out of the car, to sample the ambient air. Sharp bends were avoided and the total length of tubing was around 0.5 m per instrument. Flow rates for the CPC and Aethalometer were set at 100 cm^3/min and 150 cm^3/min, respectively. Furthermore, the PET glass and the top of the car were covered with conductive foil to counteract the electrostatic capture of particles. Two car batteries were placed in the back of the car as power supply for the instruments. Standard operating procedures were used according to manufacturer's specifications.

Quality control included zero checks and regular co-located measurements with all instruments in an indoor facility in the lab in Utrecht. Co-located measurements were performed for 2-3 days before and after all six measurement campaigns for about 6 hours per day. All instruments were positioned next to each other. The inlets of all devices were attached to a tube that was connected to a box with a small fan to mix the air.

Monitoring campagne

Measurements were taken between 9:00-16:00 (avoiding the rush hour) to obtain comparable concentrations between sites. At sampling days measurements were done at eight pre-selected sites, consequently requiring 10 measurement days per city per season to visit all 80 (81) sites. The sequence of sites visited in a day was arranged such that different site types were measured at different times of the day. Moreover, routes were spread across the cities to restrict the impact of temporal variation on the concentrations measured in a certain neighborhood. Because the study will be used for human exposure assessment, measurements were conducted close to the facade of homes. The instruments in the back of the car measured continuously during the whole day. Before and after the 30-minute sampling period, a high efficiency particulate air (HEPA) filter was attached to the CPC for a zero measurement to define the start and end of the site measurement.

Reference site

To be able to correct for temporal variation, a reference site was set up just outside the University campus of Utrecht, located in the outskirts of the city. One reference site was selected in the center of the country to be able to combine measurements from Amsterdam and Rotterdam using a single source for temporal correction. The specific site was chosen close to our laboratory. The reference site was situated about 39 km away from the center of Amsterdam and 50 km from the center of Rotterdam. To minimize the influence of traffic, the site was located in a rural area, in the garden of a house. Previously this site was used as reference site for the ESCAPE and VE^{3}SPA projects.[7,15] Concentrations at this site were monitored during all sampling days, using the same devices and methods as for the short-term measurements. The instruments were installed in a bike trailer with the same tube length and sample height as at the short-term monitoring sites. The trailer was brought to the reference site every measurement day and retrieved at the end of the day.

Data for the weather conditions were retrieved from the Royal Dutch Meteorological Institute (KNMI, the Netherlands) from nearby stations Schiphol (for Amsterdam) and Rotterdam A summary can be found in the supplemental information (SI Table S3).

Data analysis

Data cleaning

We evaluated the basic 1-sec (UFP) and 1-minute (BC) data. If the ratio of the UFP concentration and the UFP concentration measured at the next

second was above 10 or below 0.10 the measurement was considered unreliable and deleted, following previous studies.[16,17] Application of the criterion was needed in less than 0.01% of the observations. Additionally, if the ultrafine particle concentration was below 500 particles per cm^3 the data was removed, since this is very likely an artefact. Less than 1% of the reference UFP measurement and 0.05% of the UFP measurements at the short-term sites was deleted because of UFP concentrations below 500 particles/cm^3. These observations occurred connected to CPC readings of zero related to low alcohol in the CPC.

No data cleaning was performed for BC. We did not use a recently developed noise reduction method,[18] as we use 30-minute concentrations in further calculations. For all 30-minute periods, the change in attenuation was substantially larger than 0.05, the value used in the Hagler-method to redefine the time base. As the Hagler method averages the uncorrected BC concentrations for the new time base, application of this method would not have any effect on our 30-minute data. We further note that there was little noise in the 1-minute data, less than 5% of the 1-minute values were negative. Small negative values (< 1 $\mu g/m^3$) were retained.

BC concentrations may be underestimated with increasing attenuation.[19] We did not apply correction procedures reported previously,[19,20] because the correction factors differed almost two-fold between studies and between seasons in the Virrkula study. Attenuation factors in our study never exceeded 100, the set maximum of the instrument, and 91% of the data had attenuation factors below 75 used by Dons (2012) to delete observations.[21] The consequence may be some additional error in the data, but as the various site types were visited on each sampling day and in random order, no bias in comparison between site types occurred. The additional error affects within- and between-site variation similarly, as the same site may be measured with low and high attenuation in the three seasons.

All further calculations were performed with the 30-minute average at each site. We used the 30-minute mean instead of the 30-minute median to better reflect the impact of relatively infrequent sources, e.g. ships and road traffic for background locations.

Missing Data

Missing data at the reference site due to equipment failure occurred for 6% (UFP) and 20% (BC) of the observations. As this implied that we could not correct the monitoring site measurements for temporal variation, we evaluated whether we could impute reference site missing values, exploiting the often high temporal correlation at nearby sites. As UFP and BC concentrations were not measured in the National Air Quality monitoring network, we evaluated the correlation of BC/UFP at the reference sites with NO_2, NO_x and PM_{10} measurements. BC was imputed using PM_{10} at the nearby regional background site Cabauw:

BC (ng/m^3) = -173.8 + 46.2 * PM_{10} ($\mu g/m^3$) (adjusted R^2= 0.62).

Ultrafine particles had a very low correlation with all PM_{10}, NO_2 and NO_x measurements (adjusted R^2 below 0.05). Consequently, no missing data were imputed for ultrafine particles.
Equipment failure was responsible for some missing data at the short-term monitoring sites, a few sites therefore have 2 measurements instead of 3 and 1 site in Rotterdam had only 1 BC sample. For 88% (BC) and 89% (UFP) of the sites three measurements were available. Missing measurements at the short-term monitoring sites were not imputed.

Co-located measurements

The median ratios of co-located instrument readings were determined per co-location day. To correct for differences between instruments, the median ratios of the 2 to 3 co-located measurements prior to and immediately after a field campaign were multiplied with the reference site concentrations for that campaign. For BC the corrections were done per instrument number, because four different Aethalometers were used during the study. The ratios and correlations can be found in SI Tables S4 and S5.

Correction for temporal variation

To estimate the average concentration per site, the three 30-minute mean concentrations were averaged, after correcting for temporal variation using measurements from the reference site. To evaluate how well the temporal variation at the short-term monitoring sites was reflected by the reference site for these short-term samples, the correlation between the measurements at the sites and the corresponding 30-minute reference site measurement was calculated per site. The correlation coefficient for an individual site is not robust, as it is based upon three samples. However, the median of the individual correlations is more robust and was used for interpretation.

We used the difference method for correction.[6,7] In this method, the overall mean concentration at the reference site ($C_{ref,\ avg}$) was determined and then the 30 minutes measurement at time t at the reference site ($C_{ref,\ t}$) was subtracted to calculate the difference ($C_{diff\ ref,\ t} = C_{ref,\ avg} - C_{ref,\ t}$). Next, this difference was added to the 30-minutes mean concentration at short-term monitoring site x to obtain the corrected concentration at time t ($C_{x,t,\ corr} = C_{x,t} + C_{diff,\ ref,t}$). A comparison with the ratio correction method used by some other researchers is provided in SI Table S6.[8]

Evaluation of within and between-site variance of concentrations

Analysis of variance was used to obtain the estimated within- and between-site components of variance. The variance ratio was calculated by dividing the estimated within-sites by the between-sites variance for all sites with three valid measurements. For comparison, the same analysis of variance was performed with data from the ESCAPE, RUPIOH and VE^{3}SPA studies.[7,5,15] These studies involved much longer sampling times at each site (14 days for ESCAPE, 24 hour for RUPIOH and 96 hour for VE^{3}SPA) and were thus expected to have smaller within-sites/between-sites variance ratios. For RUPIOH, sampling was continuous for one week. To avoid autocorrelation, we included 24-hour average UFP concentrations measured at the 1st, 4th and 7th day for the variance component analyses for the RUPIOH data. The analysis of variance was performed with uncorrected and corrected concentrations to evaluate the effectiveness of the correction procedure.
Using the variance components, we calculated the repeatability of the spatial contrast between sites expressed as the intra-class correlation coefficient (ICC).[23] We calculated the ICC for single measurements as the ratio of between-site variance and the sum of between and within-site variance: var(site) / (var(site) + var(error)). We further calculated the ICC for the average of the three repeats because the average is used in further modelling, using the formula $ICC_{avg,\ k=3}$ = var(site) / (var(site) + var(error)/k). To investigate how many repeats are needed to achieve similar repeatability of the average of the campaigns with longer duration, we also calculated the ICC for 5 and 10 repeats.

Table 1 The median temporal Pearson R between individual 30-minute mean concentrations at the short-term monitoring sites and the reference site.

			All sites			
Component	**Pooled**		**Amsterdam**		**Rotterdam**	
	Median	N	Median	N	Median	N
UFP	0.50	113	0.43	67	0.67	46
BC	0.85	141	0.76	80	0.89	61
			Without traffic sites			
Component	**Pooled**		**Amsterdam**		**Rotterdam**	
	Median	**N**	**Median**	**N**	**Median**	**N**
UFP	0.74	63	0.56	38	0.80	25
BC	0.91	82	0.92	45	0.90	37

Only sites with 3 measurements included (N=number of sites)

Concentration variability

The concentration variability between different site types was investigated by a general linear model of the natural logarithms of the mean site concentrations with site type as independent variable. The urban background sites were used as the reference category. The exponent of the slopes in the model can be interpreted as concentration ratios and represents the contrast between site types.

Results

Figure 2 illustrates the large temporal variability of the individual 30-minute average concentrations at the reference site, both between and within days. The temporal variation at the reference site was highly correlated with the corresponding 30-minute BC concentrations at the short-term monitoring sites (Table 1). The temporal correlation for UFP was lower than for BC, suggesting that correction may be less effective for UFP than for BC. The correlation was highest for the background sites, suggesting that correction is more effective for these sites than for the traffic sites.

Within and between-site variance of concentration and correction for temporal variation

The estimated within and between-site variance components are shown in Table 2. For BC, the within-sites variance component, corrected for temporal variation, was 2.44 times larger than the between-sites variance component. For UFP, the within-sites variance component was 2.17 times larger than the between-sites variance component. The variance ratio decreased after adjusting for temporal variation for BC but not for UFP. In comparison, the within-site components of variance in the ESCAPE and VE^{3}SPA study for Black Carbon, and in the RUPIOH study for UFP were much lower than the between-site components of variance, whereas the between-site components of variance were more comparable between studies. The pattern of variance ratios followed the sampling duration, with progressively higher within-sites variances with shorter sampling times (Table 2).

Furthermore the decrease in variance ratio in the RUPIOH, VE^{3}SPA and ESCAPE studies after correction for temporal variation was larger than in the current short-term monitoring campaign, indicating that the correction was more effective in the studies with longer sampling periods.
Intraclass correlation (ICC) calculated from the variance components for single observations were low for the short-term monitoring campaign (Table 2), indicating that a single measurement does not represent the spatial contrast well. The ICC of the average of three repeats was moderate for the short-term campaigns and high to very high for the longer duration

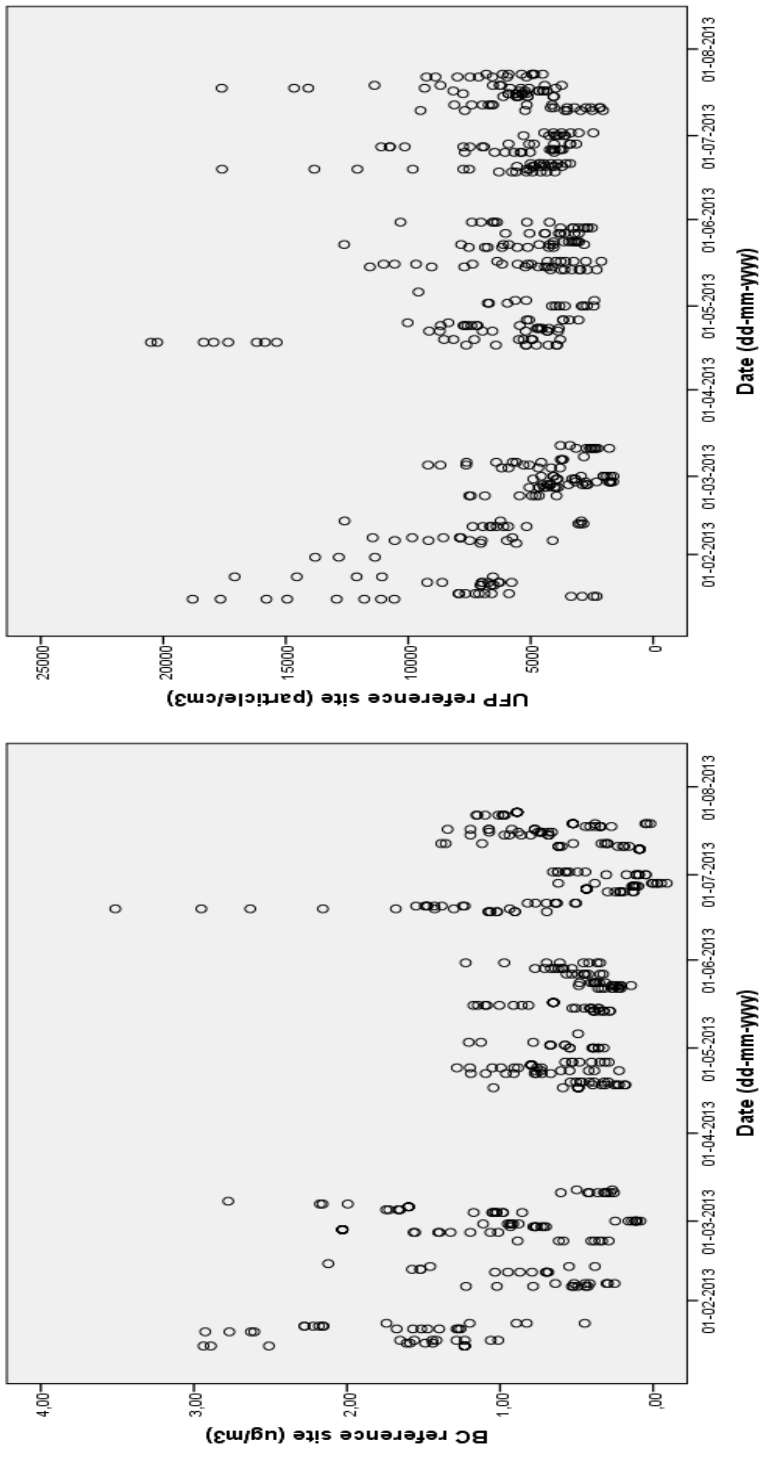


Figure 2 Temporal variability of 30-minute average BC (µg/m^3) and UFP (cm^{-3}) at the reference site

campaigns. More than 10 repeats are needed to achieve similar ICC values for the average as obtained in longer duration campaigns.
Within-site variance was much larger for street sites than for urban background sites: 1.28 vs 0.39 μg/m^3 for BC and 38*10^6 vs 20*10^6 cm^3 for UFP. Between-site variance was much larger for street sites for BC (0.41 vs 0.03) and UFP (11*10^6 vs 5*10^6). The variance ratio for street sites was lower for BC (3.1 vs 14.7) and similar for UFP (3.4 vs 3.6). The lower within-site variance for background sites suggests that fewer repetitions could be considered for these sites in future campaigns.

Table 2 Within and between site outdoor concentration variance for BC and UFP in relation to sample duration.

Project	Duration	Repeats	Components	Var(Error)[a]	Var(site)[b]	Variance Ratio[c]	ICC single	ICC Avg k=3	ICC Avg, k=5	ICC Avg, k=10
MUSiC	30 minutes	3	Corr BC	0.76	0.31	2.44	0.29	0.55	0.67	0.80
			BC	1.12	0.35	3.25	0.24	0.48	0.61	0.75
			Corr UFP	26.E6	12.E6	2.17	0.31	0.58	0.70	0.82
			UFP	31.E6	14.E6	2.21	0.32	0.58	0.70	0.82
ESCAPE	14 days	3	Corr $PM_{2.5}$ abs	0.03	0.29	0.09	0.92	0.97	0.98	0.99
			$PM_{2.5}$ abs	0.11	0.27	0.39	0.72	0.88	0.93	0.96
RUPIOH	24 hour	3	Corr UFP	89.E6	285.E6	0.31	0.76	0.91	0.94	0.97
			UFP	123.E6	244.E6	0.50	0.67	0.86	0.91	0.95
VE^{3}SPA	96 hour	6	Corr $PM_{2.5}$ abs	0.08	0.11	0.69	0.59	0.81	0.88	0.94
			$PM_{2.5}$ abs	0.23	0.09	2.55	0.28	0.54	0.66	0.80

BC in μg/m^3 , UFP in (particles/cm^3). $PM_{2.5}$ abs (10^{-5} m^{-1}) is a surrogate for BC (μg/m^3). ICC = intra class correlation coefficient for single measurements and average (avg) of k observations (calculated for 3, 5 and 10 repeats). ICC calculated as var(site) / (var(site) + var(error)) for single observations and var(site) / (var(site) + var(error)/k) for average. Sample duration is for individual samples. Corr is corrected for temporal variation using the difference method. BC and UFP are uncorrected. In ESCAPE Netherlands, 37 sites had 3 samples. In VE^{3}SPA, 13 out of 15 sites had 6 samples. [a] within site concentration variance [b] between site variance [c] within/between site variance

Spatial contrast across site types

Table 3 shows that the mean UFP and BC concentrations were higher at the street sites in both cities. Increases compared to urban background sites were similar for BC and UFP. UFP but not BC concentrations were increased at highway sites. The mean concentrations of UFP and BC measured were

lowest at the regional sites. Furthermore, the contrast between the different site types, with the urban background sites as reference is shown. The overall mean concentration of UFP at the reference site was 5,825 particles/cm^3 and 0.80 µg/m^3 for BC. This was 1.43 and 1.22 times lower than the pooled concentrations at regional sites for UFP and BC, respectively.

Table 3 Distribution of average concentrations of ultrafine particles and black carbon per site type

Amsterdam									
		UFP (particles/cm^3)				**BC (µg/m^3)**			
Site type	**N**	**Mean**	**(Min - Max)**	**SD**	**Ratio**	**Mean**	**(Min - Max)**	**SD**	**Ratio**
Green	9	11606	(6611 - 20806)	4273	1.19	1.07	(0.89 - 1.47)	0.21	1.02
Highway	3	14095	(10726 - 18118)	3739	1.50’	1.12	(0.93 - 1.39)	0.24	1.07
Region	4	7860	(6890 - 9039)	910	0.85	0.80	(0.45 - 1.59)	0.54	0.67*
Street	32	17051	(6636 - 57897)	9698	1.66*	1.93	(0.88 - 5.67)	1.00	1.69*
Urban	28	9587	(5282 - 16082)	2826	1.00	1.09	(0.62 - 2.33)	0.39	1.00
Water	5	8583	(5346 - 11126)	2245	0.91	0.92	(0.46 - 1.15)	0.27	0.85
Rotterdam									
		UFP (particles/cm^3)				**BC (µg/m^3)**			
Site type	**N**	**Mean**	**(Min - Max)**	**SD**	**Ratio**	**Mean**	**(Min - Max)**	**SD**	**Ratio**
Green	5	8827	(6039 - 14080)	3269	0.89	0.95	(0.80 - 1.09)	0.12	0.90
Highway	2	14827	(11879 - 17776)	4170	1.53	1.02	(0.66 - 1.39)	0.51	0.92
Region	4	8910	(4902 - 11886)	3087	0.89	1.37	(0.81 - 2.01)	0.55	1.24
Street	29	13713	(5034 - 23414)	5176	1.33*	1.73	(0.59 - 3.68)	0.78	1.50*
Urban	32	10104	(4910 - 17144)	3565	1.00	1.10	(0.40 - 2.21)	0.36	1.00
Water	8	10993	(6180 - 15241)	2887	1.12	1.36	(0.70 - 0.00)	0.58	1.21
Pooled									
		UFP (particles/cm^3)				**BC (µg/m^3)**			
Site type	**N**	**Mean**	**(Min - Max)**	**SD**	**Ratio**	**Mean**	**(Min - Max)**	**SD**	**Ratio**
Green	14	10614	(6039 - 20806)	4054	1.07	1.03	(0.80 - 1.47)	0.19	0.98
Highway	5	14388	(10726 - 18118)	3391	1.50	1.08	(0.66 - 1.39)	0.31	1.01
Region	8	8385	(4902 - 11886)	2180	0.87	1.09	(0.45 - 2.01)	0.59	0.91
street	61	15464	(5034 - 57897)	7995	1.49*	1.83	(0.59 - 5.67)	0.90	1.60*
Urban	60	9863	(4910 - 17144)	3225	1.00	1.09	(0.40 - 2.33)	0.37	1.00
Water	13	10066	(5346 - 15241)	2834	1.03	1.19	(0.46 - 2.28)	0.52	1.06

Concentrations are averages of the three 30-minute samples corrected for temporal variation using the difference method. SD is the standard deviation. Ratio is the ratio with the urban background sites as the reference sites, calculated as the exponential Beta of the lnUFP/lnBC general linear model

*significant at the p<0.05 level ‘significant at the p<0.10 level

Figure 3 The distribution of corrected UFP site mean concentrations (counts/cm³) per site type. Box indicates 25th and 75th percentile, horizontal line in box is median. Individual observations shown if more than 1.5 (°) or 3 (*) times the interquartile range away from the box. Site mean is average of up to three 30-minute mean concentrations.

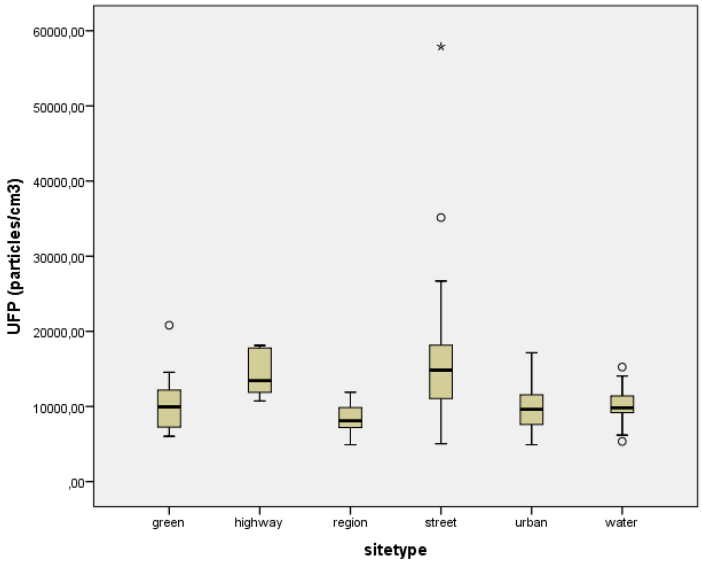
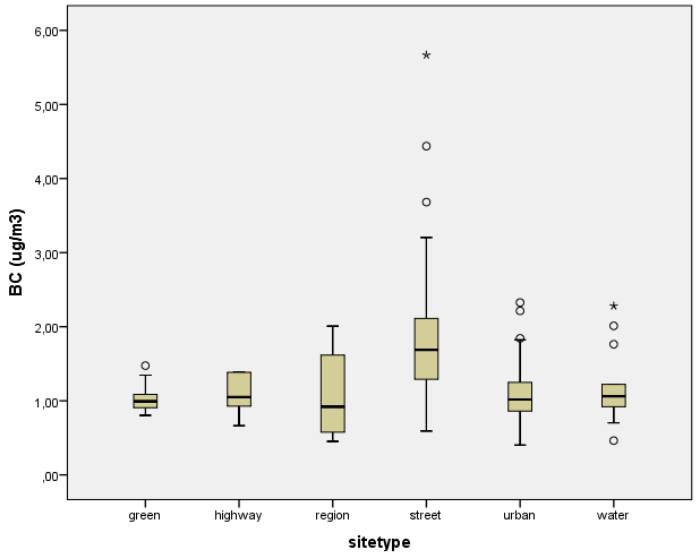


Figure 4 The distribution of BC site mean concentrations (µg/m³) per site type. Box indicates 25th and 75th percentile, horizontal line in box is median. Individual observations shown if they are more than 1.5 (°) or 3 (*) times the interquartile range away from the box. Site mean is average of up to three 30-minute mean concentrations.



The spatial variation of the UFP and BC concentrations is the highest between different street sites (Figures 2 and 3). The highest individual mean concentration was measured at site A17 for both components. This site was located in the center of Amsterdam, close to a traffic light (29 m) with stop and go traffic.

Discussion

Ambient UFP and BC concentrations were measured for 30 minutes in three different seasons at 161 locations to assess spatial variation in two cities. Within to between-site variance ratios were larger than unity. Variance ratios were much larger than calculated for previous campaigns with sampling periods of 24 hours to 14 days. Correction for temporal variation was less effective than for the studies with longer sampling periods. The BC and UFP concentrations at street locations were on average 1.60 and 1.49 times higher, respectively, than at urban background sites.

Temporal variation correction

Measurements were not taken simultaneously but sequentially in the field, because only one mobile platform was available. Therefore, temporal variation in concentrations needed to be accounted for. Previous studies had documented substantial temporal variation of short-term variation of UFP both between and within sampling days.[10,11,14] To restrict the impact of temporal variation, continuous BC and UFP measurements were done at a reference site. The within to between-site variance ratio was substantially decreased for BC, but much less so for UFP. This is consistent with the lower temporal correlation between reference site and short-term sampling sites (Table 1), indicating that the reference site was less representative for temporal variations of UFP. A possible explanation might be that UFP are more reactive than BC, therefore local circumstances have more influence on UFP than on BC concentrations. Another explanation is that UFP may be more dominated by local sources. A potential problem might be that the reference site may have been less representative for temporal variation in the study areas, because it was situated in Utrecht, located 35-50 km away from the two monitoring cities. However, the pattern of lower correlations between reference and field measurements for UFP than for BC was also observed in a study of four cities where the reference site was located within the city, suggesting that local variation plays a more important role than the location of the reference site.[24] The temporal correlation between a central site and residential outdoor sites 24-hour average concentrations in Amsterdam was 0.76 for UFP and 0.94 for $PM_{2.5}$ absorbance measured as an integrated 24-hour sample in that study.[24] The correlation for hourly UFP concentrations was lower than for 24-hour averages (0.66 in Amsterdam), supporting the hypothesis that

temporal correction will be less effective for shorter sampling times.[24] Our correlation is similar to the correlation observed in Amsterdam and the other three cities for hourly observations. The lower correlation for 30-minute averages compared to 24-hour averages is likely explained by larger impact of short-duration local sources (e.g. higher than usual traffic intensity) or weather conditions (e.g. wind direction). With short-duration sampling, the air parcels affecting different sites are furthermore different. In a study in the Boston area, the temporal correlation of UFP measurements at 18 homes with three central monitors was between 0.45 and 0.73.[25] The location of the reference site in a nearby suburban area in our study likely does not fully explain the lower correlation for UFP compared to BC in our study.

Within to between-site variance ratios

The variance ratios for BC and UFP were larger than two, reflecting a higher within-site variation than between-site variation. In RUPIOH and ESCAPE, studies with longer sample times, the variance ratios were lower than one. In ESCAPE, samples were taken during 2 weeks in 3 seasons at 40 sites in the Netherlands and Belgium.[7] For RUPIOH 3 samples of each 24 hours in one week at 50 sites in Amsterdam were used for our comparison.[22] For MUSiC, the UFP ratio was 4.2 times larger compared to RUPIOH and the BC ratio was 8.3 times larger than $PM_{2.5}$ absorbance in ESCAPE. The short sampling times of the mobile campaign made it possible to sample more sites than in previous campaigns. However, the shorter sampling duration resulted in a very substantial increase of within-site variation when compared to previous campaigns. With the same number of repeats, the precision of the site-specific mean will thus be substantially lower than in previous campaigns. To improve precision, future mobile campaigns could increase the number of repeats and/or increase the sampling duration per individual sample. Based upon the calculation of the intra-class correlation coefficient for the average of k repeats, more than 10 repeats are needed to approach the repeatability of the campaigns with longer duration. This number of repeats is difficult to achieve.

The ratio of variance components for UFP may be affected by the size fraction measured by the CPC 3007: particles larger than 10 nm. With the CPC 3007 particles of 10 nm are detected with 50% efficiency and particles of 18 nm with 100% efficiency.[26] Particles of 10 nm and smaller likely have higher spatial and possibly temporal variation as their fraction in fresh (traffic) emissions may be higher and the distance decay faster.[5,13]

Implications for land use regression models

When these site-specific mean concentrations are used to develop land use regression models, the larger number of monitoring sites to develop models may partly outweigh the loss in precision in establishing mean

concentrations. In land use regression models, the site-specific mean is used as the dependent variable with traffic and land use predictors as the independent variables. Traffic and land use variables are typically fixed, that is they differ spatially between sites but not temporally. Insufficient correction of temporal variation from the average concentration data, can be viewed as measurement error. Measurement error in a continuous dependent variable does not result in biased regression coefficients but it does result in a loss in precision and power.[27] Hence, in a study with a limited sample size, the influence of important predictors on concentrations may not be detected as statistically significant. Furthermore, even when the identified model may be correct, the explained variance of the model will be lower if more measurement error is present in the dependent variable. This is likely one explanation for the fairly low explained variances of land use regression models reported in the literature that are based upon mobile or short-term monitoring campaigns.[2,10,14]

Spatial variation

The average ratio between street and urban background sites was 1.49 and 1.60 for UFP and BC concentrations, respectively. The street to urban background concentration ratio in the Dutch ESCAPE campaign was 1.52 for $PM_{2.5}$ absorbance.[7] In a Dutch study conducted between June 2008 and January 2009, UFP was measured at 2 street sites and 2 corresponding background sites and $PM_{2.5}$ absorbance at 8 street sites and corresponding background sites.[28] The average street/urban background concentration ratio for $PM_{2.5}$ absorbance was 1.9 with a range of 1.5 to 2.2, with the higher ratio found for street canyons and streets with buildings on one side of the street. UFP street/background ratios were 1.3 and 2.4 with the highest ratio for the one-sided built street. The UFP ratios were almost the same as the ratios for $PM_{2.5}$ absorbance in the same streets, similar to our observations. Average UFP concentrations in the two streets (16,191 and 10,443 particles per cm^3) also agreed well with our measurements. In a study conducted for one month in the fall of 2008, mean UFP and $PM_{2.5}$ absorbance concentration at the street site in Utrecht was 3 times higher than at the urban background location.[17] In that study, the mean UFP concentration at the street site was 38,635 particles/cm^3 and at city background sites 14,094 particles/cm^3. The overall higher concentrations found in the 2008 study could be due to the configuration of the street site (homes on one side of the street only), different weather conditions in the relatively short autumn campaign and the different sampling period from noon to 6 pm including the evening rush hour. In Amsterdam in the RUPIOH study, 24-hour average PNC and $PM_{2.5}$ absorbance concentrations at 22 traffic sites were on average 1.9 and 1.4 times higher than at the central urban background site. Average PNC concentrations were much higher in RUPIOH (18,090 particles/cm^3 for the central urban background and >30,000 particles/cm^3 for the street sites), possibly related to differ-

ent equipment (CPC3022 vs CPC 3007 in the current study) and trends in time. Our average concentration at urban background agrees well with the overall average of 24 previous urban monitoring studies of 10,800 p/cm^3.[29] The review documents a large variability of UFP concentrations within major roads, often at substantially higher levels than measured in our study.[29]

For our five highway sites, we found (non-significantly) increased UFP and no increased BC concentrations relative to the urban background sites. The low contrast compared to previous studies near highways is probably due to the siting of the highway sites with (noise) barriers between site and highway and the low fraction of wind from the highway to the site (Table S2).[4,9] Short-term campaigns with short sampling duration and a small number of repeats are probably not effective for highway sites because of the strong dependence on wind direction during sampling. In contrast, measurements in urban streets in the compact Dutch urban areas are less dependent on wind direction. For near-highway communities, on-road mobile monitoring with a significant number of repeats has been successful to characterize spatial variation.[9,13]

We developed a short-term campaign to assess spatial variation for UFP. We added BC to be able to assess the specificity of the UFP spatial contrasts. We found a squared correlation of 0.62 between the average UFP and BC concentration which suggests that the established UFP spatial pattern does not fully mirror a BC pattern in the cities. The correlation is higher than the correlation reported for 2-minute average concentrations in a study in a near-freeway neighborhood near Boston (Spearman R^2= 0.39), but lower than reported for the RUPIOH study in Amsterdam based on fixed sampling with longer duration (R=0.85).[9,22] The difference likely reflects the impact of temporal variation on the compared concentrations, as temporal correlations between UFP and BC may be low. In our study the temporal correlation between UFP and BC at the reference site was 0.10.

Conclusion

Within to between-site concentration variance ratios for BC and UFP were larger than two. These variance ratios were much larger than for previous campaigns with sampling periods of 24 hours to 14 days (variance ratios of 0.09 to 0.77). Correction for temporal variation was less effective than for the studies with longer sampling periods. The implication for the use of the site-specific mean concentration as dependent variable in land use regression studies is loss in precision and low explained variance of the models. To achieve the same repeatability of the average as for the campaigns with 24 hour to 14 day sampling times, more than 10 repeats

are needed. An alternative is to increase the sampling duration. The BC and UFP concentrations at street locations were on average 1.60 and 1.49 times higher than at urban background sites.

References

1. Hoek, G.; Boogaard, H.; Knol, A., et al Concentration response functions for ultrafine particles and all-cause mortality and hospital admissions: Results of a European expert panel elicitation. Environmental Science and Technology 2010, 44, 476-482.

2. Larson, T.; Hernderson, S.; Brauer, M. Mobile monitoring of particle light absorption coefficient in an urban area as a basis for land use regression. - Environ Sci Technol 2009, 4672-4678.

3. De Hartog, J.J.; Hoek, G.; Mirme, A., et al Relationship between different size classes of particulate matter and meteorology in three European cities. J. Environ. Monit. 2005, 7, 302-310.

4. HEI Review Panel Understanding the Health Effects of Ambient Ultrafine Particles Report . Health Effects Institute 2013, January, HEI Perspectives 3.

5. Zhu, Y.; Hinds, W.C.; Kim, S.; Sioutas, C. Concentration and size distribution of ultrafine particles near a major highway. Journal of the Air and Waste Management Association 2002, 52, 1032-1042.

6. Hoek, G.; Meliefste, K.; Cyrys, J., et al Spatial variability of fine particle concentrations in three European areas. Atmos. Environ. 2002, 36, 4077-4088.

7. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. Atmospheric Environment 2012, 62, 303-317.

8. Merbitz, H.; Fritz, S.; Schneider, C. Mobile measurements and regression modeling of the spatial particulate matter variability in an urban area. Sci. Total Environ. 2012, 438, 389-403.

9. Padró-Martínez, L.T.; Patton, A.P.; Trull, J.B.; Zamore, W.; Brugge, D.; Durant, J.L. Mobile monitoring of particle number concentration and other traffic-related air pollutants in a near-highway neighborhood over the course of a year. Atmos. Environ. 2012, 61, 253-264.

10. Rivera, M.; Basagaña, X.; Aguilera, I., et al Spatial distribution of ultrafine particles in urban settings: A land use regression model. Atmos. Environ. 2012, 54, 657-666.

11. Peters, J.; Theunis, J.; Van Poppel, M.; Berghmans, P. Monitoring PM10 and ultrafine particles in urban environments using mobile measurements. Aerosol and Air Quality Research 2013, 13, 509-522.

12. Li, L.; Wu, J.; Hudda, N.; Sioutas, C.; Fruin, S.A.; Delfino, R.J. Modeling the concentrations of on-road air pollutants in Southern California. Environmental Science and Technology 2013, 47, 9291-9299.

13. Kozawa, K.H.; Winer, A.M.; Fruin, S.A. Ultrafine particle size distributions near free-

ways: Effects of differing wind directions on exposure. Atmos. Environ. 2012, 63, 250-260.

14. Abernethy, R.C.; Allen, R.W.; McKendry, I.G.; Brauer, M. A Land Use Regression Model for Ultrafine Particles in Vancouver, Canada. Environ. Sci. Technol. 2013, 47, 5217–5225.

15. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Agreement of land use regression models with personal exposure measurements of particulate matter and nitrogen oxides air pollution. Environ. Sci. Technol. 2013, 47, 8523-8531.

16. Strak, M.; Steenhof, M.; Godri, K.J., et al Variation in characteristics of ambient particulate matter at eight locations in the Netherlands - The RAPTES project. Atmos. Environ. 2011, 45, 4442-4453.

17. Boogaard, H.; Montagne, D.R.; Brandenburg, A.P.; Meliefste, K.; Hoek, G. Comparison of short-term exposure to particle number, PM10 and soot concentrations on three (sub) urban locations. Sci. Total Environ. 2010, 408, 4403-4411.

18. Hagler, G.S.W.; Thoma, E.D.; Baldauf, R.W.; Long, T.R.; Snow, R.F. Impact of meteorology, traffic characteristics, and distance from roadway on roadside concentrations of ultrafine particulate matter. Proceedings of the Air and Waste Management Association's Annual Conference and Exhibition, AWMA 2008, 1, 151-156.

19. Virkkula, A.; Mäkelä, T.; Hillamo, R., et al A simple procedure for correcting loading effects of aethalometer data. Journal of the Air and Waste Management Association 2007, 57, 1214-1222.

20. Apte, J.S.; Kirchstetter, T.W.; Reich, A.H., et al Concentrations of fine, ultrafine, and black carbon particles in auto-rickshaws in New Delhi, India. Atmos. Environ. 2011, 45, 4470-4480.

21. Dons, E.; Int Panis, L.; Van Poppel, M.; Theunis, J.; Wets, G. Personal exposure to Black Carbon in transport microenvironments. Atmos. Environ. 2012, 55, 392-398.

22. Hoek, G.; Beelen, R.; Kos, G., et al Land use regression model for ultrafine particles in Amsterdam. Environ. Sci. Technol. 2011, 45, 622-628.

23. Armstrong B.K., White E, Saracci R. Principles of exposure measurement in epidemiology. Monographs in Epidemiology and Biostatistics. Oxford University Press 1992, 21,

24. Puustinen, A.; Hämeri, K.; Pekkanen, J., et al Spatial variation of particle number and mass over four European cities. Atmos. Environ. 2007, 41, 6622-6636.

25. Fuller, C.H.; Brugge, D.; Williams, P.L.; Mittleman, M.A.; Durant, J.L.; Spengler, J.D. Estimation of ultrafine particle concentrations at near-highway residences using data from local and central monitors. Atmos. Environ. 2012, 57, 257-265.

26. Mordas, G.; Manninen, H.E.; Petëjä, T.; Aalto, P.P.; Hämeri, K.; Kulmala, M. On operation of the ultra-fine water-based CPC TSI 3786 and comparison with other TSI models (TSI 3776, TSI 3772, TSI 3025, TSI 3010, TSI 3007). Aerosol Science and Technology 2008, 42, 152-158.

27. Armstrong, B.G. Effect of measurement error on epidemiological studies of environmental and occupational exposures. Occup. Environ. Med. 1998, 55, 651-656.

28. Boogaard, H.; Kos, G.P.A.; Weijers, E.P., et al Contrast in air pollution components between major streets and background locations: Particulate matter mass, black carbon, elemental composition, nitrogen oxide and ultrafine particle number. Atmos. Environ. 2011, 45, 650-658.

29. Morawska, L.; Ristovski, Z.; Jayaratne, E.R.; Keogh, D.U.; Ling, X. Ambient nano and ultrafine particles from motor vehicle emissions: Characteristics, ambient processing and implications on human exposure. Atmos. Environ. 2008, 42, 8113-8138.

Supplemental Information

Site Descriptions

During the 30 minute site measurements, traffic was counted for 15 minutes in both directions. The 15-minute traffic counts were multiplied by 48 (4*12) to account for daytime traffic. Daytime traffic is 78% of the total traffic per 24 hours, therefore multiplying by 1.29 (=1/0.78) gives the traffic intensities per 24 hour.[1] At each site (except highway sites) the passing vehicles were counted during all three 30-minutes measurements. Table S1 shows the traffic counts for the different site types. For waterway sites the number of ships passing by were counted (3-27 and 3-12 ships per 15 minutes in Amsterdam and Rotterdam, respectively). For highway sites traffic counts were obtained from an on-line tool (http://www.saneringstool.nl/saneringstool.html). A detailed description of the situation at the highway sites during the three seasons can be found in table S2.

Figure S1 Pictures of a water site (left) and a street site (right)

Table S1 Traffic counts (vehicles/day) of site types. Nr is the number of sites per site type.

City	Type	Nr	light vehicles		Light-heavy vehicles		Heavy-heavy vehicles	
			Mean	(Min-Max)	Mean	(Min-Max)	Mean	(Min-Max)
Amsterdam	Green	9	1281	(0 - 6687)	46	(0 - 268)	8	(0 - 41)
	Highway	3	115626	(68297 - 180152)	3977	(2041 - 6012)	5085	(2819 - 7824)
	Region	4	143	(0 - 475)	4	(0 - 21)	0	(0 - 0)
	Street	32	10817	(3426 - 25986)	371	(83 - 1011)	149	(21 - 537)
	Urban	28	310	(0 - 1135)	3	(0 - 21)	2	(0 - 21)
	Water	5	674	(62 - 1775)	10	(0 - 21)	0	(0 - 0)
Rotterdam	Green	5	684	(83 - 1692)	0	(0 - 0)	13	(0 - 62)
	Highway	2	181725	(176377 - 187073)	7870	(5956 - 9784)	10571	(7734 - 13407)
	Region	4	1100	(124 - 2332)	71	(0 - 103)	0	(0 - 0)
	Street	29	14715	(2993 - 33375)	263	(21 - 619)	190	(21 - 495)
	Urban	32	1222	(21 - 10733)	19	(0 - 165)	14	(0 - 289)
	Water	8	482	(0 - 1238)	23	(0 - 124)	5	(0 - 21)

Light vehicles= the number of motorized vehicles with less than 6 wheels, except for mopeds. Light-heavy vehicles= the number of motorized vehicles with exactly six wheels. Heavy-heavy vehicles= the number of motorized vehicles with more than six wheels

Table S2 Characteristics of highway sites

Site	Date	City	Season	Distance to highway (m)	(Sound) barrier	Wind highway to site	Wind direction nearest weather station*	Infl
A65	16-5-2013	Amsterdam	spring	29	Yes, plastic	NE	N	0.5
	26-2-2013		winter			NE	NE	1
	12-7-2013		summer			NE	NW	0.25
A66	24-5-2013		spring	30	Trees	S	NW	1
	1-3-2013		winter			S	N	0
	18-7-2013		summer			S	NE	0
A67	14-5-2013		spring	72	Earth wall	SE	NW	0
	22-2-2013		winter			SE	NE	0.25
	10-7-2013		summer			SE	S	0.5
R79	22-4-2013	Rotterdam	spring	79	Earth wall	NE	NW	0.25
	18-1-2013		winter			NE	E	0.5
	21-6-2013		summer			NE	NW	0.25
R80	17-4-2013		spring	22	Bushes	E	S	0.25
	21-1-2013		winter			E	E	1
	18-6-2013		summer			E	NW	0

*weather station 'Schiphol' for Amsterdam and weather station 'Rotterdam' for Rotterdam, the wind direction determined per hour. Infl = influence of the wind direction at the time on the site (1 is maximal influence, 0 minimal).

Weather characteristics

The hourly measurements from the nearest weather station from the KNMI (Royal Dutch Meteorological Institute) were used. For Amsterdam, the nearest weather station was "Schiphol" and for Rotterdam "Rotterdam".

Table S3 Weather characteristics during the measurement campaigns

Amsterdam										
	Temperature		**Windspeed**		**Rain**		**Humidity**		**Pressure**	
Season	**(C°)**		**(0.1 m/s)**		**(0.1 mm)**		**(%)**		**(0.1 hPa)**	
	mean	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**
Winter	3.9	(-2.1 - 15.2)	57.4	(10.0 - 100.0)	0.0	(-0.9 - 0.0)	71.1	(42.0 - 94.0)	1020.3	(999.1 - 1034.6)
Spring	12.3	(7.0 - 19.8)	60.9	(10.0 - 100.0)	1.1	(-1.0 - 18.9)	70.6	(45.4 - 95.0)	1006.7	(998.1 - 1015.8)
Summer	23.3	(16.1 - 31.3)	39.4	(10.0 - 70.0)	0.0	(0.0 - 0.0)	57.7	(35.4 - 83.0)	1022.3	(1012.1 - 1025.9)
Rotterdam										
	Temperature		**Windspeed**		**Rain**		**Humidity**		**Pressure**	
Season	**(C°)**		**(0.1 m/s)**		**(0.1 mm)**		**(%)**		**(0.1 hPa)**	
	mean	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**	**mean**	**(min - max)**
Winter	-0.3	(-6.5 - 7.5)	45.8	(11.8 - 120.0)	0.6	(-1.0 - 12.8)	77.7	(59.0 - 95.8)	1009.0	(997.6 - 1025.4)
Spring	13.5	(6.8 - 20.4)	59.3	(19.8 - 160.0)	0.9	(-1.0 - 22.0)	70.2	(50.0 - 97.0)	1019.7	(1011.5 - 1026.1)
Summer	18.9	(13.8 - 29.4)	43.8	(14.4 - 80.0)	0.5	(-1.0 - 23.0)	67.9	(44.2 - 95.0)	1018.2	(1008.8 - 1029.4)

Co-located measurements

The co-located measurements were used to check the comparability of the instruments. After outliers and incorrect measurements were deleted, regression analyses were done for each co-located measurement day to determine the correlation between instruments. Correlations of the co-located measurements can be found in Table S4.

Table S4 Correlations of the co-located measurements. The median, first (Q1) and third (Q3) quartile Pearson's R^2

	Median (Q1 - Q3)
UFP	0.92 (0.70 - 0.98)
BC	0.55 (0.40 - 0.95)

The daily median ratios of the co-located measurements indicate that the ratio's differed more between the different co-located measurement campaigns than between the days of a single campaign (data not shown). Therefore, to adjust for differences between the instruments, the median ratios of the co-located measurements prior to and immediately after a certain field campaign were used. First, the ratios per individual continuous measurement were calculated. Next the median ratio per day was determined. The median ratios of these 2-3 median co-located measurement ratios prior to and immediately after a certain field campaign were multiplied with the reference site concentrations for that campaign. For BC the adjustments were done per instrument number, because four different Aethalometers were used during the study and during different seasons. Table S5 shows the median ratios used for correction of the differences between the instruments in winter, spring and summer for UFP. For example, reference site concentrations measured during the summer campaign in Rotterdam were multiplied with the corresponding seasonal ratio for that city (1.06).

Table S5 Median Ratios of the co-located measurements used for correction during the three different seasons

Amsterdam	Winter	Spring	Summer
UFP	1.42	1.09	1.04
Rotterdam	**Winter**	**Spring**	**Summer**
UFP	1.44	1.21	1.06
	397/380	397/414	414/413
BC	0.86	1.04	0.86

Temporal variation correction

In previous studies the absolute difference method and the ratio method have been used. We evaluated which method corrected for temporal variation best with the short sampling times in our study.

Difference method
The correction procedure is as follows for BC and UFP (http://www.escape-project.eu/manuals/ESCAPE_Exposure-manualv9.pdf):

1. Calculate the annual average for the reference site for the full study: cr(avg)
2. Calculate for the reference site the difference of the measurement for each 30-minute period t in which short-term measurements have been conducted from the annual average dcr(t) = cr(t) – cr(avg)
3. Subtract the difference for period t from the measurement at site i (i=1 to 161) in period t: ci , adjusted(t) = ci (t) – dcr(t)
4. Calculate the arithmetic mean of these adjusted concentrations and the standard error of the mean to document how well the mean is established

Table S6 Distribution of the standard error of the mean (SEM) relative to the site-specific mean (%) concentration before and after correction for temporal variation

Component	Percentiles	Uncorrected SEM / mean (%)	Corrected with difference method SEM / mean (%)	Corrected with ratio method SEM / mean (%)
UFP	100%	74.4	115.9	66.9
	75%	31.3	29.6	32.8
	50%	23.0	20.4	24.0
	25%	13.7	14.4	15.5
	0%	0.7	0.1	1.1
	N	159	159	159
BC	100%	255.1	169.8	167.5
	75%	47.5	33.6	46.3
	50%	33.9	20.8	27.3
	25%	21.5	11.4	15.7
	0%	1.3	0.6	-129.5
	N	160	160	160

Relative precision for each site is the standard error of the mean as a percentage of the mean. Sites with more than 1 observation only.

Figure S2 Scatterplot of corrected vs. uncorrected average of the three 30-minute average UFP (counts/cm³)

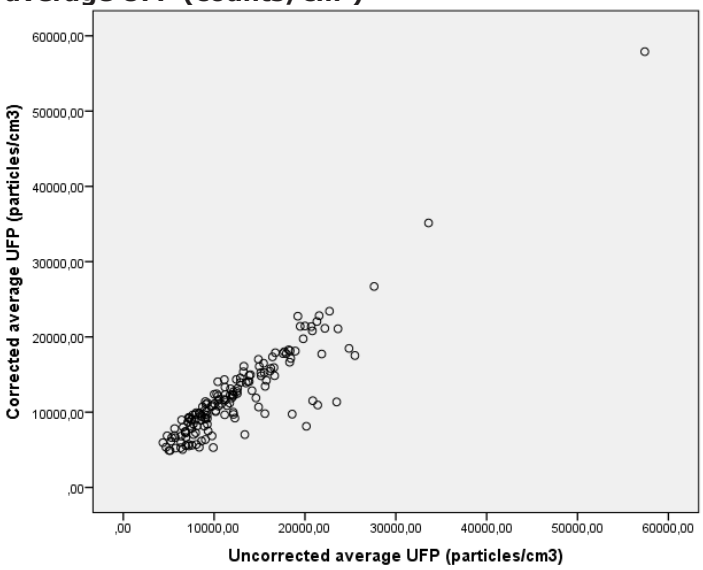
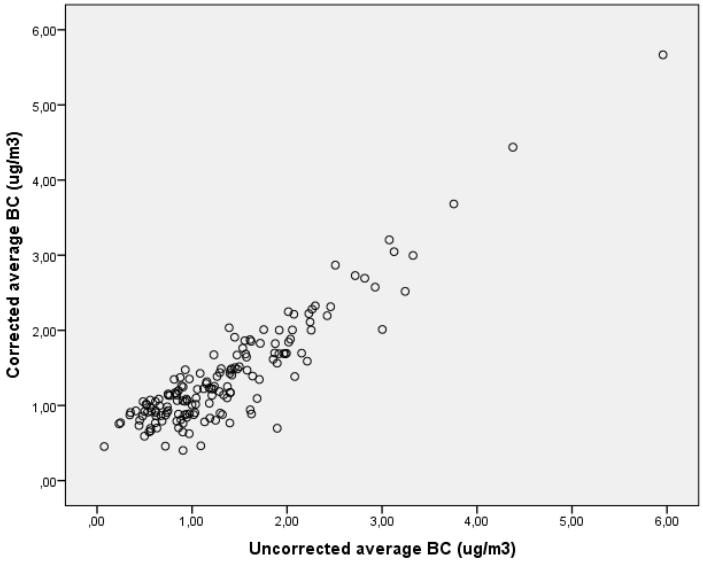


Figure S3 Scatterplot of corrected vs. uncorrected average of the three 30-minute average BC (µg/m³)



Ratio method
The adjustment procedure is similar to the difference method:

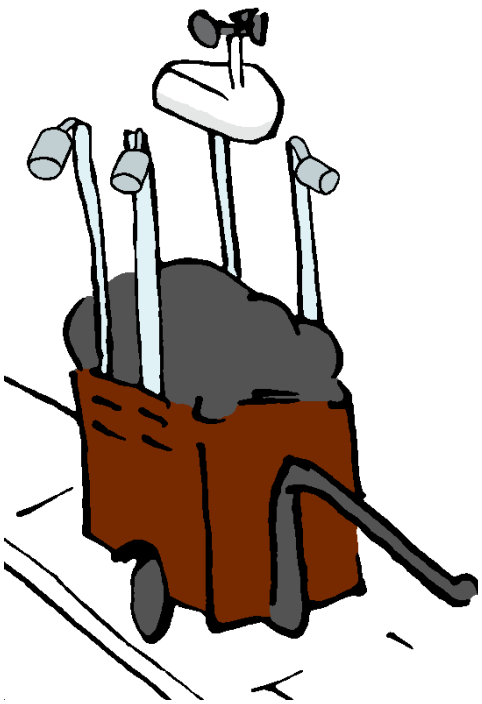
1. Calculate the annual average for the reference site for the full study: cr(avg)
2. Calculate for the reference site the ratio of the measurement for each 30-minute period t in which short-term measurements have been conducted of the annual average rcr(t) = cr(t) / cr(avg)
3. Divide the concentration for period t from the measurement at site i by the ratio for period t (i=1 to 161) in period t: ci , adjusted(t) = ci (t) / rcr(t)
4. Calculate the arithmetic mean of these adjusted concentrations and the standard error of the mean to document how well the mean is established

Results of a comparison of the two correction methods based upon the standard error of the mean is shown in table S6. The ratio correction method resulted in higher SEM than the difference method. The SEM showed a large variation between sites even when expressed as a percentage of the mean.

Adjustment for temporal variation using the difference method only had a moderate impact on the calculated mean. The correlations between uncorrected and corrected mean UFP and BC concentrations were very high, with an R^2 of 0.84 for both components (SI Figure S2 and S3).

References

1. Van Roosbroeck, S.; Jacobs, J.; Janssen, N.A.H.; Oldenwening, M.; Hoek, G.; Brunekreef, B. Long-term personal exposure to PM2.5, soot and NOx in children attending schools located near busy roads, a validation study. *Atmos. Environ*. **2007**, 41 (16), 3381-3394).



Chapter 6

Land use regression models for ultrafine particles and black carbon based on short-term monitoring predict past spatial variation

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Submitted

Abstract

Health effects of long-term exposure to ultrafine particles (UFP) have not been studied in epidemiological studies because of the lack of spatially resolved UFP exposure data. Short-term monitoring campaigns used to develop land use regression (LUR) models for UFP typically had moderate performance.

The aim was to develop and evaluate spatial and spatiotemporal LUR models for UFP and Black Carbon (BC).

We measured 30 minutes at each of 81 sites in Amsterdam and 80 in Rotterdam the Netherlands in three different seasons. Concentrations were adjusted for temporal variation using measurements at a central reference site. Models were developed using traffic, land use, reference site measurements, routinely measured pollutants and weather data.

The percentage explained variation (R^2) varied between 0.34-0.50 for BC and 0.32 - 0.43 for UFP. Traffic variables were present in every model. The coefficients for the spatial predictors were similar in spatial and spatio-temporal models. LUR models for UFP and especially BC predicted spatial contrasts from previous campaigns based on longer sampling durations well, with prediction R^2s higher than the model and hold-out validation R^2s.

Our study provides support for the use of short-term campaigns to develop spatial LUR models for UFP and BC.

Introduction

Studies of health effects of outdoor (traffic related) air pollution have focused on particulate matter with a diameter of less than 2.5 μm ($PM_{2.5}$) or 10 μm (PM_{10}), Black Carbon (BC) and nitrogen dioxide (NO_2). It has been suggested that ultrafine particles (UFP) have a high penetration rate and are biologically more reactive than larger particles.[1,2] UFP are airborne nanoparticles with a diameter less than 100 nm and account for a large fraction of the total particle number, while contributing little to ambient particle mass.[3] BC is created by incomplete combustion. BC may be a useful indicator of health effects related to particulate matter especially at the local scale.[4]

Frequently, land use regression (LUR) models are used in epidemiological studies to estimate long-term exposure to ambient air pollution for participants in such studies.[5] LUR models for particulate matter combine measurements at typically 20 – 40 locations and predictor variables (traffic, land use) in an empirical statistical model. Only a few LUR models have been developed for UFP,[6-11] because of monitoring issues such as the cost of equipment and problems related to leaving equipment unattended for periods of 1- 2 weeks, the typical duration of purpose-designed sampling campaigns. UFP is usually not monitored in routine monitoring networks. To capture the high spatial variation of UFP, most previous studies have used mobile monitoring or short-term campaigns, typically with short (15 minutes to hours rather than days to weeks) observation periods for each measurement.[6-10] The only UFP LUR model based upon fixed monitoring was derived in Amsterdam using data collected for evaluation of spatiotemporal patterns across the city in a large EU funded study.[11] In most short-term monitoring studies a site was measured only once.[6-8] These short-term measurements likely have more temporal variability and might therefore be less precise in determining spatial variation of long-term average concentrations. Another approach consists of on-road mobile monitoring with typically even shorter sampling at specific locations but more repeats.[10,12] Studies have used mobile and short-term campaigns to develop models for BC as well.[6,12] LUR models for $PM_{2.5}$ absorbance (a marker for BC) have also been developed based on study designs with sampling times of weeks.[13,14] Limited attention to independent validation of the models has been given in the mobile campaign based LUR models. Recent methodological work has shown the importance of independent validation of LUR models based upon the typically relatively small number of sites using fixed monitoring.[15-17] It is not clear whether the same applies to mobile or short-term monitoring campaigns with larger number of sites but shorter sampling durations.

The aim of the Measurements of UFP and Soot in two Cities (MUSiC) project, was to develop and evaluate LUR models for UFP and BC in Rotterdam and Amsterdam (the Netherlands) based on short-term monitoring. The second aim was to assess the validity of the LUR models in predicting previously and independently measured spatial contrasts of

UFP and BC.[11,14] The design of the monitoring campaign and an evaluation of within site temporal and between site spatial concentration variability has been reported separately.[18] The short-term monitoring study had a much higher ratio of within-site to between-site concentration variability, compared to studies with longer sampling times.[18] In the current paper several model building methods were explored to account for the high within-site temporal variability.

Methods

Study Design

The development of the LUR models involved monitoring of UFP and BC at 161 sites in Amsterdam and Rotterdam, the collection of predictor variables using a geographic information system (GIS) and regression modelling to link monitoring results and predictor variables.[5,19] We developed spatial and spatiotemporal models.

The design of the monitoring campaign has been described previously.[18] In short, in Amsterdam 81 and in Rotterdam 80 sites were selected, representing a large spatial contrast in traffic characteristics and land use. Approximately 30 sites per city were traffic sites. Other site types were urban background, regional background, urban green, highway sites and sites adjacent to water bodies. Water sites were chosen to determine the influence of ship emissions. Traffic sites were defined as sites at roads with more than 10,000 vehicles per day. Measurements were made for 30 minutes per site. Measurements were conducted at each site in three seasons; winter, spring and summer. In total, 483 measurements at 161 sites were conducted between January and July 2013. Measurements were taken between 9:30 am and 4:00 pm, to increase comparability of measurements across sites. The equipment was placed in an electrical vehicle (REVA, Mahindra Reva Electric Vehicles Pvt. Ltd., Bangalore, India). The sampling heights were around 1.5 m. During the entire measurement campaign, measurements were performed at a single reference site in Utrecht using the same sampling equipment. One reference site was selected in the center of the country to be able to combine measurements from Amsterdam and Rotterdam using a single source for temporal adjustment.

UFP was monitored each second with CPC 3007 instruments (TSI, Tenessee, USA). The CPC 3007 measures particles from 10 nm to above 1 μm and thus does not specifically measure UFP. However, UFP typically dominates total particle number counts.[3] BC was measured averaged over each minute, using the micro Aethalometer (Aethlabs, CA, USA). All further calculations use the 30-minute average concentration. QA/QC

included zero checks and co-location of instruments. More details have been reported previously.[18]

Adjustment for temporal variation

The concentrations at the reference site were used to adjust the concentrations at the short-term sites for temporal variability (day to day and within day), so that the spatial contrast between sites can be determined. First, the corresponding 30-minute mean concentration at the reference site is subtracted from the overall mean reference site concentration. This difference is added to the 30-minute mean concentration at the sites. Finally the average concentration from the three adjusted 30-minute mean concentrations per site was calculated. We previously documented that this difference method performed better than the ratio adjustment method in our study.[18]

LUR Model development

The LUR models were developed using a methodology that has previously been successfully applied in the Netherlands to model the spatial variation of the concentration of $PM_{2.5}$, NO_2 and the soot content of fine particles.[14] This methodology was developed within the framework of the European Study of Cohorts for Air Pollution Effects (ESCAPE). In brief, the mean concentrations per site were entered in a linear regression model with several GIS variables. The offered predictor variables can be found in the supplemental information (Table S1). The GIS variables were selected using a supervised stepwise selection procedure. The direction of the effect for the variables were determined a priori and the variable with the highest adjusted R^2 (coefficient of determination) was entered in the model. The next variable was added when the adjusted R^2 increased more than 1%. The variables in the resulting models were checked for p-value (removed when p-value>0.10), colinearity (Variance Inflation Factor (VIF)>3 were removed) and influential observations (if Cook's D>1 the model was further examined). The final models were evaluated by Hold-out validation (HV) and Morans' I to detect possible spatial autocorrelation in the residuals. Hold-out validation (against data from sites not included in model building) reflects the true prediction ability of LUR models to the independent locations not used for modeling. For our HV, half of the sites were randomly selected for model building and the other half were used to validate the predicted values.[17] This procedure was repeated 10 times. The datasets were stratified to ensure that half of the traffic sites were included in every training and test set.

Spatial and spatiotemporal LUR models were developed. For the spatial model site-specific adjusted averages were used following the procedure outlined above. Models were developed for Amsterdam and Rotterdam

separately and for the two cities pooled. As a sensitivity analysis we developed models with the concentrations transformed with the natural logarithm to reduce the influence of high concentrations on the model results. Furthermore, models were developed by weighting data from all sites by their inverse standard error of the mean, giving sites for which the mean was estimated more precisely a higher weight in the regression analysis. Sites with <2 samples were excluded from all analyses, resulting in the exclusion of one site for BC and two different sites for UFP.
Spatiotemporal models were developed using the individual unadjusted 30-minute mean measurements, with different temporal predictors in the model to account for temporal variation. We evaluated the corresponding reference site 30-minute mean concentrations, weather data from the nearest weather station and NO_2 measurements in the cities at routine urban background stations and combinations of these predictors. To further interpret differences between spatial and spatiotemporal models, a fixed spatiotemporal model was developed, always including the spatial variables from the pooled spatial models.
The coefficients for each predictor in the final models were multiplied with the difference between the 90th and the 10th percentile of the predictor variable to compare the impact of predictors with different variability on the concentrations.

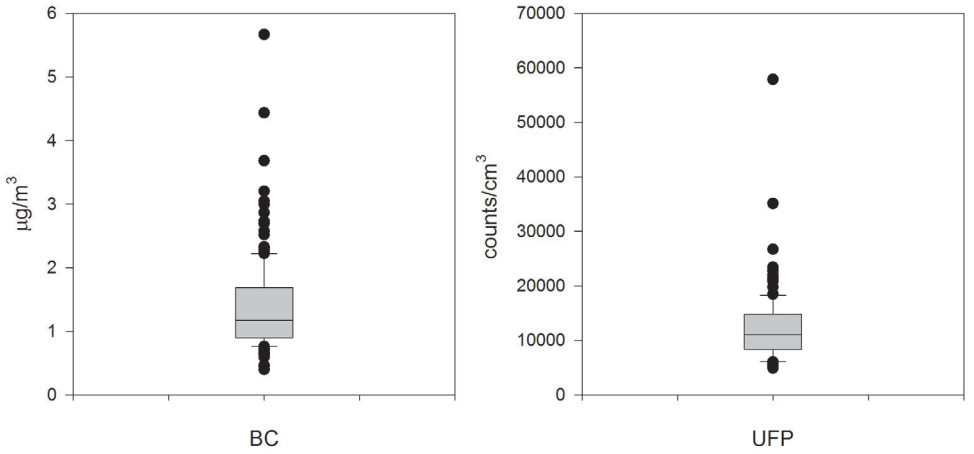
Comparison with previously measured concentrations

To further assess the ability of the developed LUR models to predict spatial concentration contrasts at sites not used in model development, we collected data from two previous Dutch LUR studies, ESCAPE and RUPIOH.[11,14] In the ESCAPE study, annual average $PM_{2.5}$ absorbance concentrations were measured at 40 monitoring sites spread over the Netherlands / Belgium. The averages were based upon three 14-day average concentrations measured in three seasons in 2009 and adjusted for temporal variation using the same reference site as in the current study.[14] In the RUPIOH study, averages were based upon at most seven 24-hour average UFP concentrations at 48 locations across Amsterdam between October 2002 and April 2004, adjusted for temporal variation using UFP data from an urban background reference site in the city.[11] LUR model predictions were compared with past measured adjusted average concentrations.

Results

Figure 1 shows boxplots of the adjusted mean UFP and BC concentrations at the 161 sites. The spatial variation has been described in detail previously.[18]

Figure 1 Boxplot of BC (µg/m³) and UFP (counts/cm³) concentrations (adjusted average per site) N=161



Spatial models per city

The LUR models for UFP and BC, adjusted for temporal variations using the measurements at the reference site, in Amsterdam and Rotterdam are described in Table 1. The models for the unadjusted concentrations can be found in the supplemental information, Table S2. The Cook's D test showed no influential observations. All Moran's I values were small and generally non-significant indicating no evidence of spatial autocorrelation.

For the Rotterdam UFP model there was statistically significant spatial autocorrelation but with a near-zero Moran's I of 0.013.
The percentage of explained variation (R^2) for BC was 0.40 and 0.41 in Amsterdam and Rotterdam. For UFP R^2 was 0.33 and 0.42 in Amsterdam and Rotterdam, respectively. The model R^2 was similar to models based upon concentrations unadjusted for temporal variation (Table S2). Model structures differed only mildly between adjusted and unadjusted concentrations.
The population variable within a 5000 meter buffer was present in Rotterdam and Amsterdam models, both for UFP and BC. The models included 2-4 variables and every model included traffic variables. As indicated by the coefficients multiplied by the difference between the 90th and the 10th percentile of predictors, the models predict sizable contrasts.
In Amsterdam, the training set models from the HV predicted 16% less variation for BC and 13% for UFP in the test sets compared to the full model R^2. In Rotterdam the gap between the full model R^2 and HV was larger, 26% for BC and 22% for UFP. Absolute values for HV R^2 were low for all models.

Table 1 LUR models for the adjusted average BC and UFP concentrations per city

Component City	LUR model[a]	R^2 of model	HV median[b] (min-max) R^2	Number of sites[c]	Mean (min-max) measured concentrations
BC ($\mu g/m^3$)					
Amsterdam	0.46 + TRAFNEAR*0.53 + DISTINVMAJORC1*0.38 + POPEEA_5000*0.42	0.40	0.24 (0.11-0.45)	81	1.39 (0.45-5.67)
Rotterdam	0.46 + MAJORROADLENGTH_50*0.67 + POPEEA_5000*0.56 + DISTINVMAJORC2*0.16 + INDUSTRY_500*0.01	0.41	0.15 (0.08-0.27)	79	1.36 (0.40-3.68)
UFP ($counts/cm^3$)					
Amsterdam	4171.58 + DISTINVMAJORC1*6308.30 + POPEEA_5000*4373.31	0.33	0.20 (0.13-0.45)	80	12780 (5282-57897)
Rotterdam	4648.25 + HEAVYTRAFNEAR*1579.78 + MAJOR-ROADLENGTH_50*3886.54 + POPEEA_5000*4443.03	0.42	0.20 (0.12-0.28)	79	11480 (4902-23414)

a.Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors.
See SI (Table S1) for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters. The following predictors were derived: the surface area (m^2) of low density residential land (LDRES_X), industry (INDUSTRY_X), port (PORT_X), population (POPEEA_X), total length (m) of all road and all major road segments (ROADLENGTH_X, MAJORROADLENGTH_X), inverse distance (m^{-1}) and inverse squared distance (m^{-2}) to the nearest major road in the central network (DISTINVMAJORC1, DISTINVMAJORC2), traffic intensity on the nearest road (TRAFNEAR) and nearest major road (TRAFMAJOR), heavy traffic intensity on the nearest road (HEAVYTRAFNEAR), the sum of (traffic intensity × the length of all road segments) within a buffer ($vehicles \cdot day^{-1} \cdot m$) for roads (TRAFLOAD_X).
b. Hold-out Validation median (minimum-maximum) R^2 of the correlation of the 10 training set models predictions for the test sets
c. Number of sites that have been used for model development.

Table 2 Pooled LUR models for the adjusted average BC (µg/m³) and UFP (counts/cm³) concentrations

Component	LUR model[a]	R^2 model	HV median[b] (min-max) R^2	Number of sites[c]	Mean (min-max) measured
BC	0.62 + DISTINVMAJORC1*0.52 + TRAFNEAR*0.30 + POPEEA_5000*0.37	0.35	0.24 (0.12-0.39)	160	1.38 (0.40-5.67)
UFP	3220.77 + DISTINVMAJORC1*4552.02 + POPEEA_5000*3959.36 + TRAFLOAD_100*1739.90 + PORT_5000*2255.38	0.37	0.29 (0.19-0.48)	159	12134 (4902-57897)

a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors. See SI (Table S1) and Table 1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters.
b. Hold-out Validation median (minimum-maximum) R^2 of the correlation of the 10 training set models predictions for the test sets
c. Number of sites that have been used for model development.

Table 3 Spatiotemporal LUR models for BC and UFP, including temporal and spatial variables (bold)

Component	LUR model[a]	R^2 model	HV median[b] (min-max) R^2	Nr of samples[c]	Mean (min-max)
BC (µg/m³)	-0.71 + NO_2_ROUTINE*1.13 + DISTINVMAJORC1*0.47 + REFBC*0.92 + TRAFNEAR*0.44 + TEMP*0.59	0.50	0.21 (0.08-0.30)	446*	1.42 (-0.23-6.26)
UFP (counts/cm³)	2303.69 + DISTINVMAJORC1*4362.17 + REFUFP*5355.17 + NO_2_ROUTINE*5780.94 + POPEEA_1000*3820.58 + RELHUM*-2811.52 + TRAFLOAD_100*1602.63	0.39	0.26 (0.16-0.38)	417*	12885 (3259-43193)

* The measurements at the network and the reference site had some missing data
a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors. See SI (Table S5) and Table 1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters. UFP measurements at the reference site (REFUFP), NO_2 measurements at the continuous monitoring sites from routine networks (NO_2_ROUTINE).
b. Hold-out Validation median (minimum-maximum) R^2 of the correlation of the 10 training set models predictions for the test sets
c. Number of samples used for model development.

Spatial pooled models

Table 2 shows the LUR models for the pooled adjusted BC and UFP concentrations. The models for the unadjusted concentrations can be found in the Supporting information Table S3. As with the separate city models, the R^2 of the adjusted BC and UFP models did not improve when compared to the unadjusted models. The explained variation for the pooled model was slightly lower than the R^2 for the models per city for BC and in between for UFP. The pooled BC model included three and the UFP model four variables. For BC, the population variable and the inverse distance to the nearest major road were present in both city models and persisted in the pooled model, with a slope that was comparable to the slope in the Amsterdam model.
For UFP, only the population variable was present in all three models with similar slopes. Furthermore, the pooled model contained two traffic variables and a variable for port area.
For both BC and UFP, the gap between the full model R^2 and the HV test set predictions was around 10%, substantially lower than for the city-specific models. Absolute HV values were higher than for the city-specific models but remained low.
When the concentrations were natural log transformed, the explained variance was 0.41 and 0.42 for BC and UFP respectively (Table S4). In the log transformed BC model the population variable was replaced by the similar low density residential land variable and the model included two additional variables, port area in a 5000 m buffer and road length in a 50 m buffer. The variables included in the ln UFP model were equal to the pooled model with untransformed concentrations. The slopes in the ln model have a different interpretation, e.g. the slope of 0.30 for TRAFNEAR in the BC model predicts a 35% increase in BC concentration for an increase of TRAFNEAR of 21,159 vehicles/day (the difference between 90^{th} and 10^{th} percentile).

For BC the R^2 of a model weighted by the inverse standard error of the mean of the site-specific measurements was marginally larger (6%) than for the pooled models (Supporting Information, Table S5). For UFP the weighted model had 3% lower explained variability. In both the BC and UFP models one of the sites was excluded because of a Cooks D value>3.

Spatiotemporal models

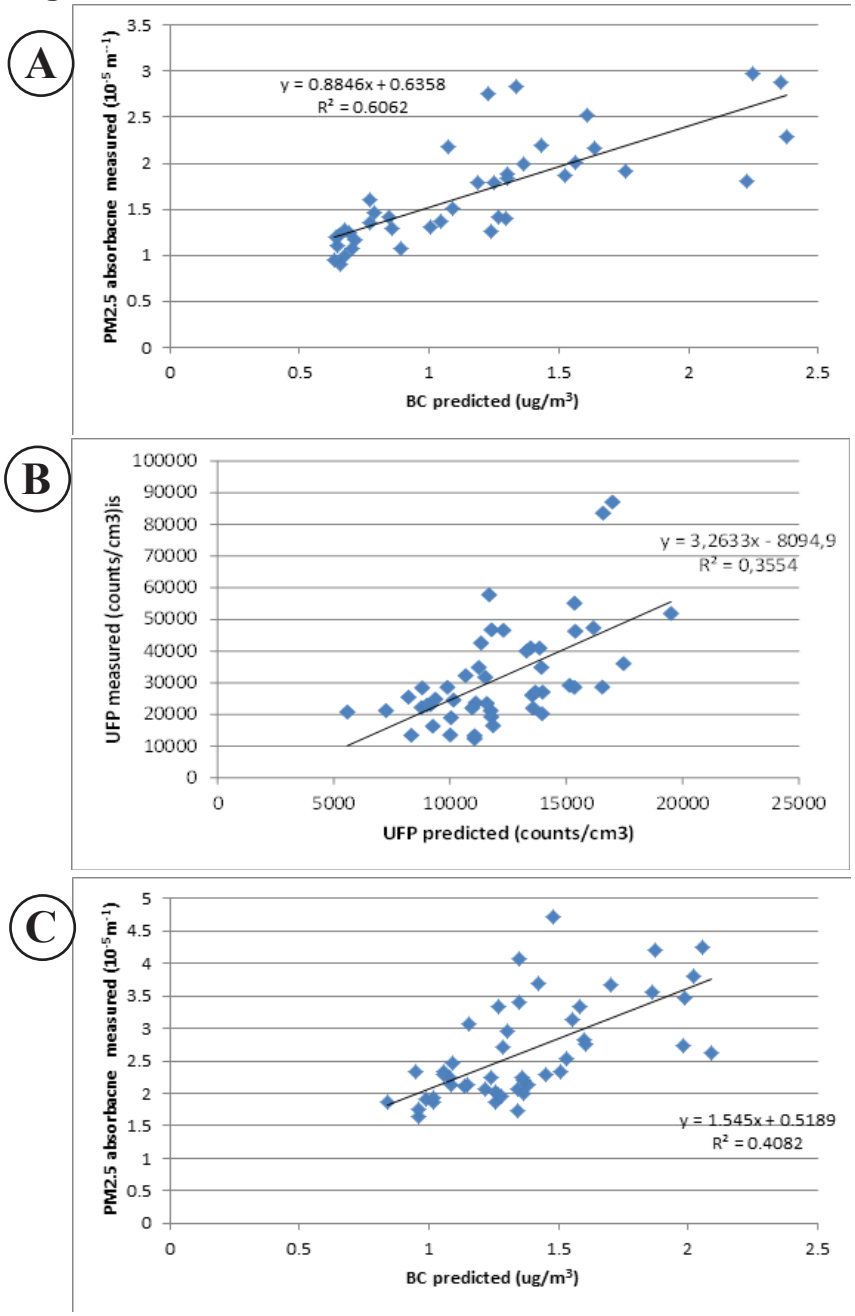
In Table 3 and Table S6, the spatiotemporal LUR models are described. The model R^2s were very similar to the pooled spatial models. The BC model included two spatial and three temporal variables. The variables inverse distance to the nearest major road (m^{-1}) and traffic intensity on the nearest road were present in the pooled spatial and in the spatiotemporal model. The slopes for both variables had similar magnitude as

in the pooled models. The population variable of the spatial model was not included in the spatiotemporal model, because it did not add more than 1% explained variability. When forced into the model, the slope of the population variable was only 22% lower than the slope of the pooled model (Table S6). The gap between the full model R^2 and the median HV R^2 was 29%, substantially larger than for the pooled spatial model.
For UFP, three spatial and three temporal variables were included in the model. The three spatial variables were identical (inverse distance to the nearest major road and traffic load within a buffer of 100 meters) or similar (population in a 1000 m buffer instead of a 5000 m buffer) to the pooled spatial model. The port variable of the spatial model was not included in the spatio-temporal model and had a smaller slope when forced into the model (Table S6). For UFP the 13% difference between full model and HV R^2 was larger than for the pooled spatial model difference (8%).
The best spatiotemporal models for UFP (BC) were developed with the UFP (BC) measured at the reference site in Utrecht, the NO_2 concentration from routine monitoring within Amsterdam or Rotterdam and weather data as temporal predictors. Models with only the reference site measurement or routinely measured NO_2 had R^2 values of 0.32 to 0.33 for both components (SI Table S6), substantially lower than the full model (Table 3). The spatial component of the models were similar between models.
When the temporal and spatial variables from the models were regressed separately, the temporal variables explained 31% and the spatial 15% of the BC variability. For UFP the temporal variables explained 12% and the spatial variables 17%.

Prediction of previously measured spatial contrasts

The pooled spatial BC model predicted spatial variation of $PM_{2.5}$ absorbance at 40 sites measured in 2009 across the Netherlands very well (Figure 2a). Remarkably, the R^2 of 0.61 was larger than the model R^2 and the hold-out validation R^2. Absolute concentration levels cannot be directly compared because of the different metrics. The pooled UFP model predicted spatial variation at 48 sites measured in 2002-2004 in Amsterdam fairly well (Figure 2b). The R^2 of 0.36 was similar to the model R^2 and higher than the hold-out validation R^2. Absolute concentration levels were much higher in the 2002-2004 campaign than predicted by the model. The model developed for Amsterdam specifically (Table 1) resulted in a slightly lower R^2 of 0.33. The log transformed model predicted the same variability with an R^2 of 0.36. The pooled BC model predicted annual average $PM_{2.5}$ absorbance across the Amsterdam sites better (R^2 = 0.41) than the model R^2 of 0.35 suggested (figure 2c).

Figure 2 Comparison of LUR predicted and externally measured annual average*



* Figure 2a (BC) from ESCAPE conducted at 40 sites in 2009 across the Netherlands; figure 2b and 2c (UFP and BC measured from RUPIOH study conducted in 2002-2004 at 48 sites in Amsterdam (Hoek, 2011); BC and $PM_{2.5}$ absorbacce are two highly correlated methods of measuring black carbon

Discussion

Spatial and spatiotemporal LUR models for BC and UFP were built that differed in their adjustment for temporal variation. For BC the percentage of explained variability varied between 0.34 and 0.50 and for UFP between 0.32 and 0.43. The coefficients for the spatial variables in the models were generally robust. Traffic variables were present in every model. The best spatio-temporal models were developed with measured UFP/ BC concentrations at the centrally located reference site, the NO_2 concentration from routine monitoring within Amsterdam or Rotterdam and weather data. LUR models for UFP and especially BC predicted spatial contrasts from previous campaigns based on longer sampling durations well, with R^2 higher than the model and hold-out validation R^2.

Comparison of LUR models with previous studies

Our LUR models based on short-term monitoring had only moderate model R^2 and low hold-out validation R^2, consistent with previous studies using mobile or short-term monitoring campaigns.[6-10] In a study in Vancouver, UFP LUR models were developed based on single short-term monitoring for 60 minutes at 80 sites.[7] The concentrations were adjusted for temporal variation with UFP data from four continuous measurement sites. As in our study, the models adjusted with NO_2 concentrations had similar explained variance to the ones adjusted with UFP reference site measurements. The explained variation of the spatiotemporal models varied between 0.29 and 0.53. The models considered different UFP concentration metrics, different methods for characterizing traffic (road length versus traffic density) and different buffer shapes (circular versus wind rose). The circular buffers and non-log transformed models performed best. The LOOCV showed a decrease of around 10% in the predicted ability of the models. The authors noted that the developed UFP models were remarkably similar to the previously developed RUPIOH model from Amsterdam.[7,11] Likewise, the UFP models in the current study were comparable to the Vancouver and previous Amsterdam study. All models included a port related variable, probably indicating that ship emissions and/or (truck) traffic to/from the ports contributes to the spatial variability in UFP. Furthermore, the models from our and the previous two studies include traffic-related variables.

In a study in Girona, Spain, LUR models for UFP were developed using single 15 minute measurements at 644 sites.[8] The measurements were adjusted for temporal variation with the ratio method using daily mean NO_x concentrations from a central monitor. The core LUR model explained 36% of the total UFP variation, which was similar to the explained variation in our study. A model based on the average of two repeated samples for a small subset of 25 sites showed a model R^2 of 0.72 compared to 0.47 for the single measurements, illustrating the importance of repeats.[8]

A study in New Delhi based on single 1-3 h measurements at approximately 40 sites reported a model R^2 of 0.23-0.28, largely explained by the temporal variables.[6] A study based on repeated on-road sampling in a small study area near a major highway in Sommerville, MA reported R^2 values of 0.38-0.53 for UFP using spatial and temporal variables.[10] Model R^2 was improved when spikes in concentrations likely related to pollution from nearby vehicles were removed. A study in Basel, Switzerland based on three repeats of 20-minute monitoring at 60 locations, reported a spatiotemporal model that explained 65% of the variation using predictors from GIS, field observations and temporal predictors.[19] The higher model R^2 than in other short-term studies was especially due to the better prediction by the suburban background UFP concentrations, which alone explained 38% of the variation of the 20-minute mean UFP concentrations. The relatively small size of the city and the location of a reference site within the city may explain the better prediction by reference site UFP in the Basel study compared to our study. In the RUPIOH study in Amsterdam, UFP was measured at 50 sites for 7 days.[11] The LUR model explained 67% of the UFP variability with field observations of especially distance to roads included versus 44% when only routine GIS predictors were included, illustrating the limitations of GIS predictors to characterize the sharp small-scale gradients in intra-urban UFP concentrations.[11]

Moderate explained variability of short-term monitoring campaign LUR models

The model R^2 of our and previously reported UFP and BC models based on mobile campaigns, were lower than reported for LUR models based upon longer averaging times for NO_2 and BC/EC/ $PM_{2.5}$ absorbance.[5,14,20] The model R^2s for BC in our study were substantially lower compared to the ESCAPE $PM_{2.5}$ absorbance models (Netherlands model R^2 0.92). The *first* and probably main explanation for the lower R^2 in our spatial models is the lower precision of the average concentrations compared to campaigns with longer averaging times. In our study measurements were performed for 30 minutes during three seasons, whereas in the ESCAPE study the measurements were performed for three times two weeks. The shorter sampling duration resulted in a much larger within site (temporal) variability than for the ESCAPE study.[18] In the current study, the variance ratio (within temporal/ between site spatial variation) was 2.44 for BC and 2.17 for UFP after adjusting for temporal variation versus 0.09 for $PM_{2.5}$ absorbance in ESCAPE and 0.31 for UFP in RUPIOH.[18] We further showed that the adjustment for temporal variation was less effective for the short-term campaign, consistent with the observation that the model R^2 for the adjusted measurements hardly improved compared to the models based upon unadjusted concentrations. This indicates that temporal variation remained in the adjusted average concentrations, which cannot be

modeled with fixed spatial predictors. *Secondly*, UFP may be harder to model, because of its reactivity and important local sources, resulting in high spatial and temporal variation. Some support for this explanation is provided by the previous LUR model for Amsterdam, in which the model R^2 was slightly lower for UFP than for $PM_{2.5}$ absorbance (0.67 versus 0.76).[11] *Thirdly*, models based on small datasets overestimate the predictive ability in independent test sets.[15,16,17] Fixed campaigns are typically based on fewer sites than the mobile and short-term campaigns. Validating the models with Hold-out validation (HV) instead of leave one out cross-validation (LOOCV) is preferable if the number of sites allows it. HV has not been applied much in mobile campaign LUR studies. The results from the Hold-out variation (HV) showed that the model R^2 overestimate the predictive ability by 8-13% for the pooled models based on 161 sites. This is a moderate gap, though larger than reported previously for long sampling durations with a similar number of sites.[15,16,17] Since we used 50% of the sites for validation rather than the full number of sites, it is possible that our HV R^2 underestimated the prediction ability of the full model. The HV R^2s were substantially lower than the ESCAPE Hold-out validation R^2s for NO_2 and $PM_{2.5}$ absorbance, suggesting that less overfitting related to the larger number of sampling sites in the short-term campaigns does not fully explain the lower R^2.[15]

Prediction of previous spatial contrasts

Despite the moderate model R^2, the LUR models predicted spatial contrasts of UFP and especially BC determined in fully independent studies in the past well. The percentage explained variation of the spatial contrast observed in these studies was equal (UFP) or even larger (BC) than the model R^2 in the current study and much larger than the holdout validation R^2. The explained variance is remarkably high considering the difference in time period (three and ten years prior to the current sampling campaign), differences in site selection (on the street near the façade in MUSiC versus equipment at homes with traffic locations usually measured at first floor balconies in ESCAPE and RUPIOH) and different monitoring equipment (CPC 3007 in MUSiC versus CPC 3022A in RUPIOH). For ESCAPE, the study area included the entire country, whereas the current model was developed in the two major cities only. The more precise assessment of the site-specific average concentrations due to the longer sampling duration in ESCAPE and RUPIOH likely explains the relatively high validation R^2. The findings further suggest that with a large number of short-term monitoring sites robust models can be developed that predict spatial variation (fairly) well despite the temporal variation. This is consistent with the relatively robust spatial predictor estimates in models developed within our study with different methods (spatial versus spatiotemporal, adjusted versus unadjusted averages). In the Girona study, adding hour of the day and sampling date to the model, improved the model R^2 from

36 to 51%, but the coefficients of the spatial variables were essentially unchanged.[8] It is important in the design of the sampling campaign to limit correlation between temporal and spatial variation, e.g. we specified that on a specific sampling day all major site types had to be measured and that traffic sites should not be measured exclusively in the morning but throughout the day.

The observation of a robust spatial model and a moderate R^2 fits with the effect of measurement error in continuous dependent variables in regression analysis.[21] Measurement error in a continuous dependent variable does not result in biased regression coefficients but it does result in a loss in precision and power. Thus, with a sufficiently large sample size, the identified model may be correct, but the explained variance of the model will be lower if more measurement error is present in the dependent variable. For the application in epidemiological studies of long-term exposure to air pollution, the comparison with annual averages at independent sites is more important than the model R^2.

The current LUR predicted $PM_{2.5}$ absorbance across the Netherlands in ESCAPE better than UFP and $PM_{2.5}$ absorbance in Amsterdam in RUPIOH, consistent with the longer sampling duration in ESCAPE (3 times two weeks) compared to RUPIOH (7 times 24 hour) and the resulting lower within/between concentration variance ratios. A second explanation is that the ESCAPE campaign was conducted three years before the MUSiC campaigns and the RUPIOH campaign ten years earlier. In contrast, the BC model was applied to the entire Netherlands whereas it was developed in the two major cities only; the UFP model was applied in Amsterdam, within the domain of development.

Overall, this analysis provides some support for the use of short-term campaigns to develop LUR models in spatial studies. It also suggests that spatial contrasts of UFP are relatively stable over a ten years period though absolute levels may have changed significantly, consistent with previous studies of NO_2.[22-24]

Pooled versus city-specific models

The pooled model R^2 did not improve compared to the city specific models. However, the gap between the model R^2 and the median HV R^2 was lower for the pooled models (8-11%) than for the city specific models (13-26%). This suggests that pooling the sites increases the predictive ability of the models in independent test sets. Consistently, the pooled model predicted the 2002-2004 UFP spatial contrast slightly better than the Amsterdam model based upon fewer sites, suggesting there was no benefit in developing local models based on fewer sites.

Spatial versus spatiotemporal models

The spatiotemporal models might be useful in time-series or birth cohort studies which need to predict the exposure in a shorter time frame than the annual average. The spatial component of the models was similar to the pooled spatial models.

The observation that the model R^2 improved significantly when reference site UFP (BC) was added to a model including routinely measured NO_2, supports the need for a reference site with UFP (BC) measurements. This is consistent with a previous study in which only moderate temporal correlations between UFP background measurements with other components were observed.[25] The coefficients for the spatial predictors did not differ materially between the different temporal adjustment models, suggesting that if prediction of average spatial contrasts is of interest valid models may be obtained even without a reference site for UFP or BC. If spatiotemporal contrasts are of interest, the increase in model R^2 documents the need for a specific reference site.

References

1. Oberdörster, G.; Oberdörster, E.; Oberdörster, J. Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. *Environ. Health Perspect.* **2005,** *113,* 823-839.

2. Utell, M.J. and Frampton, M.W. Acute health effects of ambient air pollution: The ultrafine particle hypothesis. *J. Aerosol Med. Deposition Clear. Eff. Lung* **2000,** *13,* 355-359.

3. HEI Review Panel. Understanding the Health Effects of Ambient Ultrafine Particles Report . *Health Effects Institute* **2013**

4. Janssen, N.A.; Hoek, G.; Simic-Lawson, M., et al Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5. *Environ. Health Perspect.* **2011,** *119,* 1691-1699.

5. Hoek, G.; Beelen, R.; de Hoogh, K., et al A review of land-use regression models to assess spatial variation of outdoor air pollution. *Atmos. Environ.* **2008,** *42,* 7561-7578.

6. Saraswat, A.; Apte, J.S.; Kandlikar, M.; Brauer, M.; Henderson, S.B.; Marshall, J.D. Spatiotemporal land use regression models of fine, ultrafine, and black carbon particulate matter in New Delhi, India. *Environmental Science and Technology* **2013,** *47,* 12903-12911.

7. Abernethy, R.C.; Allen, R.W.; McKendry, I.G.; Brauer, M. A Land Use Regression Model for Ultrafine Particles in Vancouver, Canada. *Environ. Sci. Technol.* **2013**, *47*, 5217 – 5225**.**

8. Rivera, M.; Basagaña, X.; Aguilera, I., et al Spatial distribution of ultrafine particles in urban settings: A land use regression model. *Atmos. Environ.* **2012,** *54,* 657-666.

9. Zwack, L.M.; Paciorek, C.J.; Spengler, J.D.; Levy, J.I. Characterizing local traffic contributions to particulate air pollution in street canyons using mobile monitoring techniques. *Atmos. Environ.* **2011,** *45,* 2507-2514.

10. Patton, A.P.; Collins, C.; Naumova, E.N.; Zamore, W.; Brugge, D.; Durant, J.L. An hourly regression model for ultrafine particles in a near-highway urban area. *Environmental Science and Technology* **2014,** *48,* 3272-3280.

11. Hoek, G.; Beelen, R.; Kos, G., et al Land use regression model for ultrafine particles in Amsterdam. *Environ. Sci. Technol.* **2011,** *45,* 622-628.

12. Larson, T.; Hernderson, S.; Brauer, M. Mobile monitoring of particle light absorption coefficient in an urban area as a basis for land use regression. - *Environ Sci Technol* **2009,** 4672-4678.

13. Dons, E.; Van Poppel, M.; Kochan, B.; Wets, G.; Int Panis, L. Modeling temporal and spatial variability of traffic-related air pollution: Hourly land use regression models for black carbon. *Atmos. Environ.* **2013,** *74,* 237-246.

14. Eeftens, M.; Beelen, R.; de Hoogh, K., et al Development of Land Use Regression models for PM(2.5), PM(2.5) absorbance, PM(10) and PM(coarse) in 20 European study areas; results of the ESCAPE project. *Environ. Sci. Technol.* **2012,** *46,* 11195-11205.

15. Wang, M.; Beelen, R.; Basagana, X., et al Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project. *Environ. Sci. Technol.* **2013,** *47,* 4357-4364.

16. Basagaña, X.; Rivera, M.; Aguilera, I., et al Effect of the number of measurement sites on land use regression models in estimating local air pollution. *Atmos. Environ.* **2012,** *54,* 634-642.

17. Wang, M.; Beelen, R.; Eeftens, M.; Meliefste, K.; Hoek, G.; Brunekreef, B. Systematic evaluation of land use regression models for NO 2. *Environ. Sci. Technol.* **2012,** *46,* 4481-4489.

18. Klompmaker, J.O.; Montagne, D.R.; Meliefste, K.; Hoek, G.; Brunekreef, B. Spatial variation of Ultrafine Particles and Black Carbon in two cities: results from a mobile measurement campaign. *Sci. Total Environ.* **2014,** *508C,* 266-275.

19. Ragettli, M.S., Ducret-Stich, R.E., Foraster, M., Morelli, X., Aguilera, I., Basagaña, X., Corradi, E., Ineichen, A., Tsai, M., Probst-Hensch, N., Rivera, M., Slama, R., Künzli, N., Phuleria, HC. Spatio-temporal variation of urban ultrafine particle number concentrations. *Atmos. Environ.* **2014,** *96,* 275-283.

20. Beelen, R.; Hoek, G.; Vienneau, D., et al Development of NO2 and NOx land use regression models for estimating air pollution exposure in 36 study areas in Europe - The ESCAPE project. *Atmos. Environ.* **2013,** *72,* 10-23.

21. Armstrong B.G. Effect of measurement error on epidemiological studies of environmental and occupational exposures. *Occup Environ Med.* **1998**, 55,651-656.

22 Eeftens M, Beelen R, Fischer P, Brunekreef B, Meliefste K, Hoek G. Stability of measured and modelled spatial contrasts in NO_2 over time. *Occup Environ Med* **2011,** 68, 765-770.

23. Cesaroni, G.; Porta, D.; Badaloni, C., et al Nitrogen dioxide levels estimated from land use regression models several years apart and association with mortality in a large cohort study. *Environmental Health: A Global Access Science Source* **2012,** *11,*

24. Gulliver, J.; De Hoogh, K.; Hansell, A.; Vienneau, D. Development and back-extrapolation of NO2 land use regression models for historic exposure assessment in Great Britain. *Environmental Science and Technology* **2013,** *47,* 7804-7811.

25. Paatero, P.; Aalto, P.; Picciotto, S., et al Estimating time series of aerosol particle number concentrations in the five HEAPSS cities on the basis of measured air pollution and meteorological variables. *Atmos. Environ.* **2005,** *39,* 2261-2273.

Supplemental Information

Table S1 All used predictor variables with predefined variable names, units, directions of effect, buffer sizes and the difference in the 90th-10th percentile, divided in spatial and temporal predictors[1]

Predictor variable	Variable name	Units	Direction	Buffer (m)	p90-p10
Spatial predictors					
Industry	INDUSTRY	m^2	+	100, 300, 500, 1000, 5000	0.00, 0.00, 4311, 333240, 3919442
Port	PORT	m^2	+	5000	10127981
Urban green	URBGREEN	m^2	-	1000, 5000	950222, 5683832
Semi-natural and forested areas	NATURAL	m^2	-	1000, 5000	3157, 4589082
Population data on a European level	POPEEA	m^2	+	100, 300, 500, 1000, 5000	285, 2507, 6653, 21803, 238542
Traffic intensity on nearest road	TRAFNEAR	$Veh.day^{-1}$	+		21159
Distance to nearest road	DISTINVNEAR1, DISTINVNEAR2	m^2	+		0.55, 0.38
Product of traffic intensity on nearest road & inverse of distance to the nearest road and distance squared	INTINVDIST, INTINVDIST2	$Veh.day^{-1}m^{-1}$, $Veh.day^{-1}m^{-2}$	+		2737, 721
Traffic intensity on nearest major road	TRAFMAJOR	$Veh.day^{-1}$	+		24041
Distance to nearest major road	DISTINVMAJOR1, DISTINVMAJOR2	m^2	+		0.12, 0.01
Product of traffic intensity on nearest major road & inverse of distance to the nearest major road and distance squared	INTMAJORINVDIST, INTMAJORINVDIST2	$Veh.day^{-1}m^{-1}$, $Veh.day^{-1}m^{-2}$	+		2922, 291
Total traffic load of major roads in a buffer (sum of (traffic intensity* length of all segments))	TRAFMAJORLOAD	$Veh.day^{-1}m$	+	50, 100, 300, 500, 1000	2205155, 5331567, 36513093, 96417565, 373228932
Total traffic load of roads in a buffer (sum of (traffic intensity * length of all segments))	TRAFLOAD	$Veh.day^{-1}m$	+	50, 100, 300, 500, 1000	2266046, 5690109, 39155217, 104073727, 392253448
Predictor variable	Variable name	Units	Direction	Buffer (m)	p90-p10
Heavy-duty traffic intensity on nearest road	HEAVYTRAFNEAR	$Veh.day^{-1}$	+		821.76

Table S1 continued

Predictor variable	Variable name	Units	Direction	Buffer (m)	p90-p10
Product of heavy-duty traffic intensity on nearest road and inverse of distance to the nearest road and distance squared	HEAVYINTINVDIST, HEAVYINTINVDIST2	Veh. $day^{-1}m$, $Veh.day^{-2}m$	+		120, 20
Heavy-duty traffic intensity on nearest major road	HEAVYTRAFMAJOR	$Veh.day^{-1}$	+		1620
Total heavy-duty traffic load of major roads in a buffer (sum of (heavy-duty traffic intensity*length of all segments)	HEAVYTRAFMAJORLOAD	$Veh.day^{-1}m$	+	50, 100, 300, 500, 1000	108783, 348206, 1889032, 5153832, 24655784
Total heavy-duty traffic load of all roads in a buffer (sum of (heavy-duty traffic intensity* length of all segments))	HEAVYTRAFLOAD	$Veh.day^{-1}m$	+	50, 100, 300, 500, 1000	109721, 365573, 1980262, 5597106, 23864563
Road length of all roads in a buffer	ROADLENGTH	m	+	50, 100, 300, 500, 1000	219, 704, 5288, 12267, 40729
Road length of all major roads in a buffer	MAJORROADLENGTH	m	+	50, 100, 300, 500, 1000	184, 394, 1976, 5033, 12763
Distance to nearest road, inverse distance (m^{-1}) and inverse squared distance (m^{-2})	DISTINVNEARC1, DISTINVNEARC2	m^{-1}/m^{-2}	+		0.28, 0.12
Distance to nearest major road	DISTINVMAJORC1, DISTINVMAJORC2	m^{-1}/m^{-2}	+		0.12, 0.01
Sum of variables LDRES (low density residential land) and HDRES (high density residential land)	HDLDRES	m^2	+		0.01
Sum of variables URBGREEN&NATURAL	UGNL	m^2	-	50, 100, 300, 500, 1000	0.01, 4027, 87526, 257977, 1018785
Temporal predictors					
Continuous fixed site NO_2 measurements by the RIVM (Rotterdam) and GGD (Amsterdam). RIVM is the National Institute for Public Health and the Environment. GGD is the public health service of Amsterdam.	No2RIVMGGD	$\mu g/m^3$	+		14
Continuous fixed site PM_{10} measurements by the RIVM (Rotterdam) and GGD (Amsterdam).	PM10RIVMGGD	$\mu g/m^3$	+		32

Table S1 continued

Predictor variable	Variable name	Units	Direction	Buffer (m)	p90-p10
Temperature measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	Temp	C°	+		25
Wind direction measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	Winddir				300
Wind speed measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	Wind	0.1 m/s	-		60
Rain factor variable (yes/no) determined by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	rain		-		
Mm of rain measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	rainmm	mm	-		0
Pressure measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	pressure	0.1 hPa	+		23
Relative humidity measured by the KNMI (Royal Dutch Meteorological Institute) at Schiphol (Amsterdam) and Rotterdam weather station	relhum	%	-		38
Hour of the day	Hour				
Adjusted UFP concentrations measured at the reference site	RefUFPcorr	counts/ cm^3	+		6832
Adjusted BC concentrations measured at the reference site	RefBCcorr	($\mu g/m^3$)	+		1376
Season	Season				

Table S2 LUR models for the uncorrected BC and UFP per city

Component City	LUR model[a]	R^2 of the model	Number of sites[b]	Mean (min-max)
BC (µg/m³)				
Amsterdam	0.68 + TRAFNEAR*0.45 + DISTINVMAJORC1*0.40 + POPEEA_5000*0.63 + URBGREEN_5000*-0.39	0.36	81	1.31 (0.07-5.96)
Rotterdam	0.05 + MAJORROADLENGTH_50*0.67 + POPEEA_5000*0.73 + PORT_5000*0.35 + DISTINVMAJORC2*0.17	0.42	79	1.39 (0.44-3.76)
UFP (counts/cm³)				
Amsterdam	6155.68 + DISTINVMAJORC1*6042.23 + TRAFLOAD_1000*4655.62	0.32	81	11915 (4705-57405)
Rotterdam	7889.82 + MAJORROADLENGTH_50*3790.71 + PORT_5000*4729.40 + HEAVYTRAFNEAR*1834.90	0.47	80	12852 (4364-25496)

a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors.
See Table S1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters. The following predictors were derived: urban green space (URBGREEN_X), industry (INDUSTRY_X), port (PORT_X), population (N) (POPEEA_X) or number (N) of households (HHOLD_X), total length (m) of all road and all major road segments (ROADLENGTH_X, MAJORROADLENGTH_X), inverse distance (m−1) and inverse squared distance (m−2) to the nearest road of the central road network (DISTINVNEARC1, DISTINVNEARC2) and the nearest major road in the central network (DISTINVMAJORC1, DISTINVMAJORC2), traffic intensity on the nearest road (TRAFNEAR) and nearest major road (TRAFMAJOR), heavy traffic intensity on the nearest (HEAVYTRAFNEAR) and nearest major road (HEAVYTRAFMAJOR), inverse distance (m−1) and inverse squared distance (m−2) to the nearest road of the local network (DISTINVNEAR1, DISTINVNEAR2) and the nearest major road in the local network (DISTINVMAJOR1, DISTINVMAJOR2), the sum of (traffic intensity × the length of all road segments) within a buffer (vehicles·day−1·m) for all roads (TRAFLOAD_X), for major roads (TRAFMAJORLOAD_X), for heavy traffic (HEAVYTRAFLOAD_X) and heavy traffic on major roads (HEAVYTRAFMAJORLOAD_X).
b. Number of sites that have been used for model development.

Table S3 Pooled LUR models

Component	LUR model[a]	R^2 of the model	Number of sites[b]	Mean (min-max)
BC (µg/m³)				
	0.16 + DISTINVMAJORC1*0.57 + PORT_5000*0.44 + LDRES_5000*0.43 + HEAVYTRAFNEAR*0.21	0.34	160	1.39 (0.44-3.76)
UFP (counts/cm³)				
	3867.96 + DISTINVMAJORC1*4533.95 + PORT_5000*4231.97 + TRAFMAJORLOAD_100*1814.71 + LDRES_5000*2384.30	0.33	161	12852 (4364-25496)

a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors. See SI and Table 1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters.
b. Number of sites that have been used for model development.

Table S4 Weighted LUR models

Component	LUR model[a]	R^2 of the model	Number of sites[b]	Mean (min-max)
BC (µg/m³)				
Adjusted	0.50 + MAJORROADLENGTH_50*0.56 + ROADLENGTH_300*0.18 + LDRES_5000*0.22	0.41	159*	1.38 (0.40-5.67)
Unadjusted	0.13 + MAJORROADLENGTH_50*0.77 + PORT_5000*0.56 + POPEEA_5000*0.31	0.46	160	1.39 (0.44-3.76)
UFP (counts/cm³)				
Adjusted	4970.90 + DISTINVMAJORC1*3110.77 + PORT_5000*3170.42 + POPEEA_5000*1849.38 + TRAFMAJORLOAD_100*1710.44	0.34	158**	12134 (4902-57897)
Unadjusted	4805.53 + MAJORROADLENGTH_50*4370.19 + PORT_5000*3098.77 + HEAVYTRAFNEAR*1266.42 + LDRES_5000*1638.80	0.44	161	12852.21 (4364.29-25496.36)

* Site R24 excluded because of a high Cook's D value ** Site A19 excluded because of a high Cook's D value
a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors. See SI and Table 1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters.
b. Number of sites that have been used for model development.

Table S5 Spatial-temporal LUR models, model including fixed temporal variables and the spatial variables from the uncorrected pooled models (fixed), model including measurements from a continuous monitoring site and spatial variables (continuous), model including measurements at the reference site and spatial variables (ref site)

Component	LUR model[a]	R^2 of the model	Number of samples[b]	Mean (min-max)
BC (µg/m³)				
Fixed	-1.05 + no2RIVMGGD*1.12 + RefBCcorr*0.91 + temp*0.54 + DISTINVMAJORC1*0.44 + TRAFNEAR*0.39 + POPEEA_5000*0.29	0.50	446	1.42 (-0.23-6.26)
Continuous	-0.71 + no2RIVMGGD*1.48 + DISTINVMAJORC1*0.45 + TRAFNEAR*0.38 + POPEEA_5000*0.39	0.32	447	1.42 (-0.23-6.26)
Ref site	-0.25 + RefBCcorr*1.39 + DISTINVMAJORC1*0.51 + TRAFNEAR*0.32 + LDRES_5000*0.37	0.33	462	1.42 (-0.23-6.26)
UFP (counts/cm³)				
Fixed	2278.22 + RefUFPcorr*652.52 + no2RIVMGGD*765.62 + relhum*902.68 + DISTINVMAJORC1*655.17 + POPEEA_5000*886.65 + TRAFLOAD_100*504.97 + PORT_5000*841.86	0.39	409	12885 (3259-43193)
Continuous	681.97 + no2RIVMGGD*5656.10 + DISTINVMAJORC1*4018.44 + PORT_5000*3959.77 + TRAFLOAD_100*1797.85 + LDRES_1000*6344.72	0.32	447	12885 (3259-43193)
Ref site	-1210.01 + RefUFPcorr*5975.91 + DISTINVMAJORC1*4320.71 + POPEEA_5000*3253.44 + TRAFLOAD_100*1745.63 + PORT_5000*2629.84	0.33	433	12885 (3259-43193)

a. Regression slopes were multiplied by the difference between the 10th and 90th percentile for all predictors. See SI and Table 1 for detailed explanation of the variable names. Some variables are buffers with _X indicating the radius of the buffer in meters. UFP measurements at the reference site (RefUFPcorr), NO_2 measurements at the continuous monitoring sites from the RIVM (in Rotterdam) or GGD (in Amsterdam) (no2RIVMGGD).
b. Number of samples used for model development.

Chapter 7

General Discussion

To study the health effects of air pollutants in epidemiological studies, accurate exposure assessment for the study participants is important. For this thesis, we conducted two exposure assessment projects, VE^{3}SPA and MUSiC. In the VE^{3}SPA project, personal exposure measurements were carried out and the agreement with land use regression (LUR) model predictions was determined. The LUR models predict annual average concentrations, used to study the long-term health effects of air pollution. Outdoor, indoor and personal concentrations were measured by 15 participants in Helsinki, Barcelona and Utrecht. The components of interest were $PM_{2.5}$, soot, NO_2, Cu, Zn, Fe, K, Ni, V, Si and S. In the MUSiC project, LUR models were developed for BC and UFP in Amsterdam and Rotterdam. This project was a short-term measurement campaign, sampling for 30 minutes in three different seasons at a total of 161 sites.

Main Findings

Chapter 2

The objective of this chapter was to quantify the agreement between LUR modeled concentrations and measured personal exposures for $PM_{2.5}$, soot and NO_2. The VE^{3}SPA study population existed of 45 volunteers in three cities (Helsinki, Utrecht, Barcelona). We compared the LUR predictions for outdoor annual average concentrations at the residential address with relatively long-term average personal exposure (six times 96 hours). Soot LUR models were significantly correlated with measured average outdoor and personal soot concentrations. Soot LUR models explained 39%, 44% and 20% of personal exposure variability (R^2) in Helsinki, Utrecht and Barcelona. NO_2 LUR models significantly predicted NO_2 outdoor concentrations and personal exposure in Utrecht and Helsinki. $PM_{2.5}$ models were moderately correlated to the outdoor concentrations in Utrecht and Helsinki, but not in Barcelona. No correlations were found between LUR modeled and personal $PM_{2.5}$ or NO_2 concentrations. $PM_{2.5}$ and NO_2 model predictions were correlated with personal soot, the component least affected by indoor sources. LUR modeled and measured outdoor, indoor and personal concentrations were highly correlated for all pollutants when data from the three cities was pooled.

Chapter 3

The agreement between LUR modeled concentrations and measured personal exposures for eight key $PM_{2.5}$ constituents, Cu, Zn, Fe, K, Ni, V, Si and S was quantified in the VE^{3}SPA population. LUR models predicted the within-city variation of average outdoor Cu and Fe concentrations moderately well (range in R^2 27-67% for Cu and 24-54% for Fe). The outdoor concentrations of K, Ni, S, Si, V and Zn were not well predicted. The LUR modeled concentration correlated significantly with measured

personal Fe exposure in Utrecht and Ni and V in Helsinki only. The LUR model predictions did not correlate with measured personal Cu exposure. After excluding observations with an indoor/outdoor ratio of >1.5, modeled Cu outdoor concentrations correlated with indoor concentrations in Helsinki and Utrecht and personal concentrations in Utrecht. The LUR model predictions were associated with measured outdoor, indoor and personal concentrations for all elements when the data for the three cities was pooled. Overall, the modeled within-city concentrations of $PM_{2.5}$ elemental composition did not predict measured variation in personal exposure well.

Chapter 4

In this chapter, the temporal association of personal exposure with home outdoor and with concentrations at a central site were assessed for the elemental composition of $PM_{2.5}$; Cu, Zn, Fe, K, Ni, V, Si and S. Six 96-hour samples were taken per person and used to determine the within-person correlation for all 45 participants (15 per city). Furthermore, samples were taken at a central reference site simultaneously. The temporal variation at a central site was highly correlated with personal exposure for Fe, K, Ni, S, Si, V and Zn, but not for Cu. The highest correlations (Pearson's R) were found for S and V (R between 0.87 and 0.98). Lower correlations were found for the elements Cu, Fe and Si associated with non-tailpipe traffic emissions and road dust (Pearson's R between -0.34 and 0.79). For $PM_{2.5}$ mass the R was lower (between 0.37 and 0.70). Exclusion of observations most affected by indoor sources increased the personal to central site correlations but did not fully explain differences between elements. The generally high correlation between temporal variation of the outdoor concentration and personal exposure supports the use of a central site for assessing exposure of PM components in time series studies for most elements.

Chapter 5

In this chapter we evaluated the within site (temporal) and between site (spatial) variation of UFP and BC with a short term measurement campaign. Measurements were done for 30 minutes at 161 sites, 81 in Amsterdam and 80 in Rotterdam, and repeated in three seasons. We further evaluated the effectiveness of adjusting for temporal variation with data obtained from a reference site. The precision of averaging short term samples from a relatively large number of sites compared to averaging long term samples at fewer sites was investigated. The precision of the long-term average estimates for individual sites was low, the within-sites variance being 2.17 and 2.44 times higher than the between-sites variance for UFP and BC, respectively. Studies with longer sampling times had smaller variance ratios (0.31 and 0.09 for UFP and BC), indicating a

smaller within sites variance than the variance between sites. Correction for temporal variation from a reference site was less effective for the short-term monitoring campaign compared to the campaigns with longer duration. The high within to between-site concentration variances may result in the loss of precision and low explained variance when average concentrations from short-term campaigns are used to develop land use regression models.

Chapter 6

LUR models for UFP and BC were developed based upon the mobile monitoring campaign. Concentrations were adjusted for temporal variation using measurements obtained at a central reference site. Models were developed for Amsterdam and Rotterdam separately and pooled, using traffic, land use, reference site measurements, routinely measured pollutants and weather data. The percentage explained variability (R^2) varied between 0.34-0.50 for BC and 0.32 and 0.43 for UFP. Traffic variables were present in every model. The coefficients for the spatial predictors were similar in spatial and spatiotemporal models. The highest spatiotemporal model R^2 was obtained with models including reference site UFP, routine site NO_2 and relative humidity. LUR models for UFP and especially BC predicted spatial contrasts from previous campaigns based on longer sampling durations well, with R^2 higher than the model and hold-out validation R^2. For this reason, our study provides support for the use of mobile campaigns to develop spatial LUR models which is actually stronger than one would have expected from the model R^2 and model validation R^2.

Possible reasons for low correlations of LUR model outdoor concentration predictions with personal exposure

The intra-city LUR models for annual average concentration predictions that were developed and applied within ESCAPE correlated poorly to moderately with the measured average personal exposure in this study. The rather poor correlation cannot be directly interpreted as an indication that the LUR models are unreliable estimates for personal exposure. Some issues of the validation study have to be considered first. Specifically, the following factors could have contributed to the poor agreement:

1. Limited spatial contrast
2. Random error because of the difficulty to characterize individual long-term average personal exposure
3. Low power because of the small sample size of the validation sample per city (n=15 subjects)
4. Indoor sources which affect measured indoor and personal exposure

5. Selection of study areas for the validation study
6. Poor prediction of the outdoor concentration at the residential address by the LUR model
7. Less than 100% infiltration of pollutants from outdoor to indoor air
8. Time spent by participants in other micro-environments than the home with different air pollution concentrations

The first four factors reflect methodological problems in conducting proper validation studies for long-term air pollution exposure assessment. The remaining factors explain why LUR models may not predict personal exposure well. In the following text the abovementioned points will be elaborated.

1 Limited spatial contrast

To assess the health effects of long term exposure it is most important to determine the spatial contrast between persons. In contrast, when temporal correlations are investigated, the within-person contrast is of interest. Because of high day-to-day variations in concentrations, it is relatively easy to obtain sufficient temporal contrast. This is reflected by the findings of previous studies that found significant temporal outdoor-personal correlations.[1-6] This agrees with our temporal correlations study, in which 6 samples per person provided enough contrast to show relatively high outdoor-personal correlations.[7] Within an urban setting obtaining spatial contrast is more difficult, spatial contrasts are almost always lower than temporal contrasts.

Table 1 The mean, range (minimum-maximum) and range/mean (%) for the spatial (Spat) and temporal (Temp) outdoor concentrations (spatial was adjusted and temporal unadjusted for temporal variation)

		$PM_{2.5}$ (μg/m³)			Soot (10^{-5}/5)			NO_2 (μg/m³)		
Dataset	City	Mean	(Range)	%	Mean	(Range)	%	Mean	(Range)	%
Spat	Helsinki	7.0	(5.4-8.9)	49.5	0.9	(0.6-1.4)	80.2	25.9	(17.0-40.0)	88.7
	Utrecht	15.5	(11.5-19.7)	52.9	1.4	(0.9-2.4)	107.3	34.3	(20.4-50.9)	88.8
	Barcelona	17.5	(12.6-23.1)	59.9	2.6	(1.7-3.7)	74.4	71.1	(55.3-103.1)	67.2
Temp	Helsinki	7.0	(-0.3-21.9)	314.4	0.9	(0.4-2.8)	260.7	25.0	(7.9-60.5)	210.5
	Utrecht	15.6	(2.8-33.8)	199.1	1.4	(0.3-3.5)	234.8	33.8	(8.6-89.7)	240.1
	Barcelona	17.5	(2.2-50.8)	277.0	2.6	(1.0-5.5)	170.7	71.8	(20.3-126.0)	147.1

In the VE³SPA study, the range (min-max) and the range/mean (%) for mean outdoor soot per participant (adjusted for temporal variation) was 0.6-1.4 (80%), 0.9-2.4 (107%) and 1.7-3.7 (74%) for Helsinki, Utrecht and Barcelona. For the (unadjusted) individual samples, reflecting temporal variation, the range was 0.4-2.8 (261%), 0.3-3.5 (235%) and 1.0-5.5 (171%), respectively (Table 1). For $PM_{2.5}$ the (adjusted) spatial range and range/mean (%) for these cities was 5.4-8.9 (50%), 11.5-19.7 (53%) and 12.6-23.1 (60%). The temporal variation was -0.3-21.9 (314%), 2.8-33.8 (199%) and 2.2-50.8 (277%).

In the VE[3]SPA study, the range (min-max) and the range/mean (%) for mean outdoor soot per participant (adjusted for temporal variation) was 0.6-1.4 (80%), 0.9-2.4 (107%) and 1.7-3.7 (74%) for Helsinki, Utrecht and Barcelona. For the (unadjusted) individual samples, reflecting temporal variation, the range was 0.4-2.8 (261%), 0.3-3.5 (235%) and 1.0-5.5 (171%), respectively (Table 1). For $PM_{2.5}$ the (adjusted) spatial range and range/mean (%) for these cities was 5.4-8.9 (50%), 11.5-19.7 (53%) and 12.6-23.1 (60%). The temporal variation was -0.3-21.9 (314%), 2.8-33.8 (199%) and 2.2-50.8 (277%).

The lower spatial contrasts for $PM_{2.5}$ could be explained by the source attribution for $PM_{2.5}$. Traffic is not a major source of spatial $PM_{2.5}$ concentration contrasts within a city, as fine particles have long atmospheric lifetimes (days), which results in relatively homogeneous concentrations and relatively high background concentrations within urban areas.[8,9] Elemental Carbon (EC), aka soot, is more affected by motorized traffic emissions resulting in larger intra-urban spatial contrasts.[10] For S (sulfate) in $PM_{2.5,}$ within-city spatial variation is even smaller than for $PM_{2.5}$, because sulfate is largely formed in the atmosphere with relatively slow chemical reactions.

2 Random error characterizing long-term average personal exposure

The ESCAPE LUR models predict annual average concentrations. To assess the validity of the LUR models, annual average personal exposure is needed. In practice this is not possible to measure directly as this would require study subjects to wear personal monitors for a whole year. Previous studies have often used short sampling periods for personal exposure monitoring.[11,12]

In our study longer samples were collected over longer periods of time. However, possibly the sampling time of 6 times 96 hours supplemented with adjustments for temporal variation was still not long enough to estimate annual averages precisely.
We calculated the within to between subject variance ratio of personal exposure using the individual 96-hour personal exposure measurements corrected for temporal variation at the reference site. To obtain a fully balanced dataset we included five valid observations per subject. Subjects with fewer valid samples were excluded from these calculations. We selected five observations per subject as a balance between sufficient repeats to obtain relatively stable variance ratios and a large number of subjects. From subjects with six valid repeats, we randomly selected five observations. Table 2 presents the variance ratios. Variance ratios were mostly above 1, illustrating the difficulty to obtain stable estimates of average personal exposure with a limited number of repeats. The

high variance ratios in Utrecht were related to a few (low) individual observations. Exclusion of these observations resulted in smaller variance ratios, which however were still larger than 2.

Table 2 The personal variance ratio's (within/between variance) corrected for temporal variation.

City	Component	N	Variance ratio
Helsinki	$PM_{2.5}$	13	2.1
	Soot	13	3.5
	NO_2	15	0.6
Utrecht	$PM_{2.5}$	14	17.2
	Soot	14	1.4
	NO_2	14	6.3
Barcelona	$PM_{2.5}$	11	1.4
	Soot	11	2.1
	NO_2	14	1.8

For each subject five valid samples were included. Subjects with fewer valid samples excluded. N= number of subjects

Furthermore, despite the prescribed time activity patterns variances in behavior might have influenced the personal exposures during the different sampling periods. Extending the sampling time might have made finding volunteers problematic and adding more samples possibly would have led to more drop outs.

3 Small sample size

Probably the number of volunteers did not provide sufficient power to detect low correlations as statistically significant in the within-city comparisons. With 15 participants, the R^2 had to be >0.25 to be significant. In addition to statistical significance, we also evaluated the magnitude of the correlations. In this study, we chose to focus on estimating the annual averages as well as possible. The duration of the sampling in combination with the number of samples was comparable to those used to develop the LUR models. Naturally, these extensive measurements per participant reduced the number of participants we could include in the study. The current study design took a 1 year period to complete, approximately three years of field work time (in the three cities including laboratory work and data management) and 36 pump units and $PM_{2.5}$ impactors. With nine extra pump units (cost 15.000 euros, we could have added 1 extra volunteer per measurement period per city with little extra work load. This means that within the same time frame and schedule, we could have

had 5 extra volunteers per city. With 20 participants per city a within-city R^2 of 0.20 would have been significant. This would not have been a very substantial gain in power. To detect a low R^2 of 0.10, more than 40 subjects would have been needed, clearly beyond the possibilities of this study. When the data from the three cities was pooled (45 subjects), the power of the analysis increased and we were able to detect lower correlations as being significant.

4 Indoor sources

Variations in indoor sources causes variance in the personal exposure. This reduces the correlations between the outdoor and personal concentrations, as the LUR models do not incorporate indoor sources. Particles from outdoor origin have likely different physicochemical and toxicological properties than particles from indoor sources. Therefore, separating the exposure to particles from these two sources is important.[13] For the health assessment of traffic related pollutants, the outdoor-derived particles are more relevant. Moreover, ambient pollutant levels may be more appropriate exposure estimates than total personal exposure.[14]

Important indoor sources for $PM_{2.5}$ are candles[15], resuspension, (gas) cooking and smoking.[16-18] Other sources are vacuuming, cleaning, wood burning and general activity. In the VE^{3}SPA project we tried to reduce the influence of indoor sources by excluding smokers and asking the participants not to burn candles. Nonetheless, excluding all indoor sources under normal living conditions is impossible. In addition, we cannot exclude that the participants did not follow the instructions completely, and reporting of deviations may have been incomplete. For example, perhaps candles were lit without our knowledge or participants forgot to report environmental tobacco smoke (ETS). We further evaluated agreement between model and measurements after excluding reported indoor sources such as ETS. Because of the wide spread use of gas for cooking in Utrecht and Barcelona we could not exclude gas cooking.

The relationship between indoor and outdoor concentrations can be represented by the indoor/outdoor (I/O) ratio.[19,20] We used the observed I/O ratio to assess the impact of indoor sources and found increased agreement between modeled and measured exposures for Fe and Cu after excluding observations with I/O ratios above 1.5 (chapter 3). However, not all particles from outside will infiltrate to the indoor environment, because of deposition of particles. Therefore, even if the ratio is smaller than 1, the influence of indoor sources cannot be ruled out.

Maybe if we could model indoor sources, the predictive ability of LUR models for indoor concentrations could be increased. Clougherty et al. identified three indoor-source factors (indoor combustion, cleaning and resuspension), though the factors were poorly predicted.[21] Levy et al. modeled indoor concentrations by using LUR models for the outdoor

concentrations multiplied by an infiltration factor and including indoor sources.[22] The indoor LUR models could explain 20%, 21%, and 36% of the variation in indoor NO_2, EC, and $PM_{2.5}$ levels, compared to our 5-37%, 30-64 % and 0-6%. The models including indoor sources had higher explained variability, except for soot (EC), which has fewer indoor sources. Unfortunately, in our study we did not have enough power to include indoor source factors in the model. Especially if we wanted to study the effect of more than one factor in 1 model, 15 participants per city is not enough.

5 Selection of study areas

For Helsinki and Utrecht, the area that was used to build the model in ESCAPE (the entire Netherlands+Belgium and Helsinki+Turku) was larger than the VE^{3}SPA study area. Furthermore, in ESCAPE samples were taken at 20 sites per country (40 in the Netherlands), whereas in VE^{3}SPA we measured at 15 sites per city.

Table 3 shows the standard deviations of the mean outdoor $PM_{2.5}$, soot and NO_2 concentrations per site in VE^{3}SPA and ESCAPE. VE^{3}SPA had lower standard deviations, indicating that the contrast was smaller than for ESCAPE.

Table 3 Standard deviations of measured outdoor concentrations in the ESCAPE (N=20/ 40 for NL) and VE^{3}SPA (N=15) projects

Project	City	$PM_{2.5}$ (µg/m^3)		Soot (10^{-5}/m^{-1})		NO_2 (µg/m^3)	
		SD	Mean	SD	Mean	SD	Mean
ESCAPE	Helsinki/Turku	2.4	8.8	0.4	1.1	7.8	17.8
	Netherlands/Belgium	4.0	16.5	0.6	1.6	11.8	29.5
	Barcelona	4.2	15.6	0.9	2.6	19.8	47.5
VE^{3}SPA	Helsinki	1.8	7.0	0.2	0.9	7.6	24.9
	Utrecht	2.8	15.6	0.5	1.4	10.2	34.6
	Barcelona	3.6	17.6	0.6	2.6	14.4	71.9

The smaller area probably decreased the correlations for components that are less dependent on traffic variables. For example, vanadium had a port variable and distance to the coast in the model in the Netherlands. This model is therefore difficult to translate to the Utrecht study area, because Utrecht is situated in the middle of the country and does not have any (sea) ports. While the lack of correlation for V is important for an epidemiological study conducted within the Utrecht region (such as EPIC-Prospect), it does not provide information for cohorts with a study

area covering the country (such as the birth cohort PIAMA). The spatial contrast for vanadium was not large enough to find any associations with personal exposure. In contrast, soot is thought to be more representative for traffic related air pollution, which could explain the higher correlations that were found.

6 Poor predictions for outdoor concentrations

LUR models principally predict ambient concentrations for the sites that were used for model building. Because of over-fitting, the R^2 of LUR models overestimates the predictive ability for outdoor air concentrations in external datasets. Furthermore, caution needs to be exercised when transferring LUR models to other cities or study areas.[23] The LUR models that were built within the ESCAPE framework had R squares of 80-90% for $PM_{2.5}$, NO_2 and soot. The performance of the LUR models for external datasets can be tested by hold-out validation (HV). In a HV, one part of the sites are used for model building (training set) to predict the concentrations for the remaining part of the dataset (test set). In the ESCAPE project, $PM_{2.5}$ and NO_2 were measured at 20 sites and NO_2 was measured at an additional 20 sites. The high correlation of $PM_{2.5}$ absorbance (soot) and NO_2 was used as a surrogate for the true HV, the $PM_{2.5}$/NO_2 sites were used as training sites and the NO_2-only sites were used as test sites. This HV for the ESCAPE LUR models showed that the R^2 for the test datasets dropped to 23, 75 and 77% for $PM_{2.5}$ absorbance and 40, 75 and 54% for NO_2 in Helsinki, the Netherlands and Barcelona, respectively.[24] For $PM_{2.5}$ HV using NO_2 as a surrogate was unfeasible, because the correlation between measured $PM_{2.5}$ and NO_2 was not high enough. For our external VE^{3}SPA dataset, the LUR models explained 57, 75 and 33% of the soot ($PM_{2.5}$ absorbance), 55, 82 and 49% of the NO_2 and 21, 43 and 10% of the $PM_{2.5}$ outdoor variability in Helsinki, Utrecht and Barcelona. This could indicate that for NO_2 and soot the models based on the complete training set performed as good or even slightly better in predicting outdoor concentrations in an external dataset than was predicted by the HV results (half of the sites in the training set) for Utrecht and Helsinki. The LUR models explained 10-43% of the $PM_{2.5}$ measured outdoor concentrations.

Poor predictions of outdoor concentrations was a larger issue for the LUR models for the elemental composition of $PM_{2.5}$. Especially for the non-traffic related elements, K, Ni, S, Si, and V, 8 out of 15 LUR models had low predictive ability with a model R^2 below 50%.[25] These elements are related to sources that are more difficult to characterize with land use variables available in GIS than traffic, e.g. wood smoke for K and specific industrial sources or residual oil burning for V and Ni.[25] In contrast, Cu and Fe, which are more associated with vehicle sources, showed higher model R^2 and had higher correlation with the VE^{3}SPA outdoor measurements.

7 Infiltration

The concentration of outdoor-origin indoor particles is first of all dependent on the ability of these particles to infiltrate indoors, outdoor-indoor correlations are expected to be higher with higher infiltration factors. The infiltration factor is the fraction of ambient particles that enter indoors and remain suspended.[13,20] The infiltration factor can be expressed with the following formula:

$$\frac{p_j * a_i}{a_i + k_j}$$

Where p_j is the penetration efficiency for pollutant j, a_i is the air-exchange rate for sampling session i and k is the decay rate for pollutant j.[22] The finer the particle size, the higher the penetration and thus the infiltration factor, increasing the outdoor-indoor correlation.[16] This is reflected by the higher correlation for soot than for $PM_{2.5}$ that was found in our study. Infiltration is likely more efficient for ambient soot than for $PM_{2.5}$, because soot is generally concentrated in the submicrometer particles of $PM_{2.5}$ which have high penetration and low decay losses.[26-28] Correlations between outdoor and indoor concentrations have been shown to be clearly lower for UFP particles than for fine particles.[29,30] UFP particles have lower infiltration factors because they have higher deposition than $PM_{2.5}$, but the low correlations can also be explained by the higher number of indoor sources for UFP than for $PM_{2.5}$.[18]
Factors that influence the infiltration factor are for example windows (open/closed) and the age of the building and therefore differs a lot between houses.[18,26] To illustrate this, in a study by Dons et al. indoor/outdoor correlation coefficients for BC ranged from 0.10 to 0.87 for the 8 studied residences.[31] In our study, we tried to take infiltration into account by stratifying for influential factors. They were not found to be significant, possibly because of a lack of power.

8 Time spent at other microenvironments

The most relevant for the exposure assessment in epidemiological studies is personal exposure. In our study higher correlations were found for indoor-personal than for outdoor-personal concentrations, which agrees with previous studies.[6,12] The differences between indoor and personal concentrations are mainly caused by the time that was spent in other environments than at home.

A study in Canada and South California showed modest differences in exposure estimations based upon the residential address alone and after adding mobility-based estimates.[32] In Vancouver, the potential bias of the estimate of the effect of NO_2 on a health effect measured at a continuous scale (regression coefficient) was ~16% towards the

null when using residence-based exposure estimates compared to the estimates including mobility.[32] In other words, adding the mobility data led to less underestimation health effects related to the exposure. Lanki et al. used questionnaire data in combination with outdoor measurements to estimate personal exposures of $PM_{2.5}$ and soot in elderly subjects. Personal exposures were measured for 2-13 times 24 hours by 37 participants in Amsterdam and 47 in Helsinki. Adding information about cooking, open/closed windows, time spent indoors elsewhere and ETS at home improved the personal exposure estimates.[33] Van Roosbroeck (2008) and Brunekreef (2005) found that average personal soot exposure was related to time spent in traffic.[34,35] Recent studies in Barcelona and Belgium documented significant effects of in-traffic exposures on personal exposure of NO_2 and BC as well.[36-38]

In this study, we've added the modeled concentrations for the school (child pattern) or other major indoor location (elderly pattern). Apart from the home environment, most time was spent at this "school" site. However, adding the school concentrations did not improve the models significantly, probably because of a lack of power.

Implications for epidemiology

The abovementioned points show that predicting home outdoor concentrations for participants in an epidemiological cohort remains challenging. For the traffic related component soot, the associations between LUR model predictions and home outdoor concentrations were 33-75%. The range of the explained variability was 30-64% for indoor and 20-44% for the personal concentrations. It seems that the biggest drop in explained variability was in predicting personal concentrations. This could indicate that for soot, the time spend in other micro-environments might have been the most important reason for the lower LUR-personal correlations. Recent studies have documented a substantial contribution of a relatively short time spent in traffic (in-traffic exposures) to BC exposures.[37]

For $PM_{2.5}$, the model-outdoor correlations were already weak to moderate (R^2 of 0.10-0.43), due to reasons mentioned above (likely mostly small spatial contrast within cities). Probably the main reasons for the further drop in predictive ability for indoor/personal exposure are infiltration and especially indoor sources, since any (significant) correlation with the models disappears for the indoor concentrations. The same seems to be the case for NO_2, the correlations dropped significantly for the indoor concentrations.

The developed LUR models from ESCAPE were applied in several epidemiological studies. The main results are described below.

In ESCAPE, the focus was on pooled effect estimates results, not on the

estimates from separate cohorts. If we assume that the VE^{3}SPA study areas (representing north, middle and southern Europe) are representative for the whole ESCAPE/European area, we could extrapolate our results to the pooled epidemiology results.

In the ESCAPE epidemiology studies the evidence for adverse health effects of long-term exposure to $PM_{2.5}$ was at least as strong as for soot. In the study by Beelen et al., a significantly increased hazard ratio (HR) of 1·07 (95% CI 1·02-1·13) per 5 μg/m^3 for natural-cause mortality was recorded for $PM_{2.5}$, whereas for soot it was 1·02 (95% CI 0·97-1·07).[39] Raaschou-Nielsen et al. investigated the association of lung cancer and air pollution and found an HR of 1·18 (0·96-1·46) per 5 μg/m^3 for $PM_{2.5}$.[40] For $PM_{2.5}$ absorbance (soot) an HR of 1·12 (0·88–1·42) was found per 10^{-5} m^{-1} increase. Dimakopoulou et al. did not find an association of any air pollutant with nonmalignant respiratory mortality.[41]

The finding of significant associations between LUR-modelled $PM_{2.5}$ and health within ESCAPE compared to no significant association between LUR-modelled $PM_{2.5}$ and measured personal exposure in this thesis, can be understood from the previous discussion of factors affecting agreement between modelled and measured concentrations. Most importantly, LUR models for $PM_{2.5}$ did predict measured personal soot exposure, the particle component with the least indoor sources. $PM_{2.5}$ models were able to predict the contrast in the outdoor-derived contribution to $PM_{2.5}$ personal exposure. The outdoor-derived fraction of PM is more relevant for the health assessment of traffic related air pollutants than indoor particles, which should be evaluated separately.

At the moment LUR models probably provide the best practical estimates for personal exposure to outdoor air pollutants in large study populations, but still some exposure error remains. Possibly, this has reduced the power to detect causal effects. For future studies, modeling infiltration factors, indoor sources and time activities could improve exposure estimates for cohort participants.

Elemental Composition

It is possible that some specific element in $PM_{2.5}$ is responsible for the main health effects. Transition metals, such as Fe, V, Ni, Cr and Cu, have been suggested as potential candidates based on their potential to produce reactive oxygen species (ROS) in biological tissues.[42] In our study, we did find LUR-personal correlations for Cu and Fe in Helsinki and Utrecht when samples that were highly influenced by indoor sources were excluded (indoor/outdoor Ratio>1.5). For K, Ni, S, Si, V and Zn however, the evidence that the modeled concentrations truly reflect personal exposure is sparse. Likely, poor prediction of home outdoor

concentrations by the LUR models played an important role. Hence, improving outdoor concentrations modelling for elemental constituents would be an important step forward.

Wang et al. investigated the relationship between $PM_{2.5}$ constituents and cardiovascular mortality.[43] No statistically significant associations between any of the elemental constituents of $PM_{2.5}$ that were investigated and CVD mortality were found in the pooled analysis. For Cu and Fe, this could indicate that there truly is no association with cardiovascular mortality. However, especially for the other elements exposure misclassification might have obscured any true effect.

Within versus between city

For between city variations, the LUR models for almost all components were highly correlated to personal exposure. This can be explained by the large differences in concentrations between the cities. With an increase in contrast, random misclassification in the exposure has less influence on the outcome.[44] This suggests that epidemiological studies could benefit from pooling data between study areas, thereby increasing exposure contrast.

Design of validation studies

To accurately estimate the personal exposure to outdoor-derived particles, ideally the influence of indoor sources is reduced to a minimum. However, asking volunteers not to burn candles during the sampling period is more realistic then asking them not to cook or clean. A possibility to circumvent this problem is not to sample during cleaning or cooking activities, for example by avoiding the evening hours. However, sampling only during mid-day hours might not be accurate estimates of the yearly average concentrations.

The results from our validation study showed that LUR model predictions for personal exposure worked better for components with traffic predictors in the model. For example, Ni and V had a variable for port area in the model and therefore the VE^{3}SPA study area was too small for these components. To validate LUR models for non-traffic related components, the study area should be as large as the study area of the health study. Within the Netherlands, several cohorts were included in the ESCAPE study, with different spatial coverage. The VE^{3}SPA results for Ni and V are not meaningful for the PIAMA birth cohort which is spread over virtually the entire country. However, the VE^{3}SPA results have implications for analyses within the EPIC PROSPECT study, which is based in Utrecht and surroundings, a study area very similar to the VE^{3}SPA area.
The VE^{3}SPA project has illustrated that individual validation of exposure

metrics used in epidemiological studies of long-term average air pollution exposure is challenging. Finding volunteers for the sampling campaigns, especially with enough spatial contrast, proved to be difficult. For the VE^{3}SPA project, the participants were asked to follow a pre-described time activity pattern and the pump units were placed in backpacks. This was not very convenient for the volunteers and required substantial dedication, especially because of the relatively long sampling time and large amount of repeated samples.

Recently, several efforts have been made to improve personal sampling equipment. Sample units the size of mobile phones are being developed. In the future, it might even be possible to combine these sampling units with automated GPS tracking devices and/or time activity patterns, making data collection a great deal easier. With this type of devices, increasing sampling times could be much more convenient, improving annual average estimates. Maybe a small pump-device in combination with a smart-phone app can be developed for existing smart phones, reducing production costs. This type of sampling using smart phones can be done by larger groups of people, greatly improving the power of validation studies.

Design of mobile campaigns

In the MUSiC project, LUR models for UFP and BC were developed using mobile monitoring data from 30-minute measurements at 161 sites in Amsterdam and Rotterdam in three different seasons. Few studies have developed LUR models based on fixed sites monitoring with sampling durations of longer than 24 hours.[51,52] Most studies used mobile or short-term campaigns. A study in the Girona region (Spain) measured UFP at 644 sites for 15 minutes.[46] For a subset of 25 sites the measurements were repeated, with a Pearson correlation coefficient of these repeated measurements of only 0.24. A study in Vancouver (Canada) monitored UFP at 80 sites for 1 hour.[48] This study did not include repeated sampling. In our study, the precision of using short-term measurements for estimating long-term average concentrations and of different methods to adjust for temporal variation was explored. The variance ratio's (within/between site variation) were 2.44 for BC and 2.17 for UFP, adjusted for temporal variation. This showed that the within site variation was larger than the between site variation, thus adjusting for temporal variation using measurements from the reference site was not sufficient for these short term samples. The variance ratio's for projects with longer sampling times were smaller, for example for VE^{3}SPA the adjusted ratio for soot was 0.77. Thus, to improve the *precision* of the average concentrations, sampling times need to increase and/or more repeated samples per site need to be done to reduce the influence of temporal variation. However, the models that were developed in this study using various approaches for temporal

adjustments gave robust *spatial* predictions. Likely the large number of sites provided enough spatial contrast for the GIS predictors to explain the spatial variance between the sites fairly well. This suggests that our approach of repeated 30-minute sampling in three different seasons might be effective enough to develop relatively robust LUR models. More work in other study areas is needed to confirm/ refute this suggestion. An important design aspect of our study was to limit the correlation between temporal and spatial variation by requiring that sites with different values of key predictor variables (e.g. traffic and background sites) were measured on every sampling day.

LUR models based on a small number of samples tend to overestimate the predictive ability in independent datasets.[53,54] This is supported by our study, in which the Hold-out validation for the pooled dataset showed a smaller gap (8-11%) between the model R^2 and the median HV R^2 than the individual city models (13-26%). In comparison, the gap between the model and HV R^2 was larger in ESCAPE (30-40%), with 40 sites for NO_2 and 20 for soot in the training set.[24] Increasing the number of sites in the training set improves the performance of the LUR models. When the MUSiC pooled BC model was applied to predict the soot concentrations measured in 2008-2010 at the ESCAPE sites, the R^2 of the association was 0.61. The MUSiC pooled UFP model was able to predict the concentrations measured in 2002-2004 at the RUPIOH sites with an R^2 of 0.35, which was very similar to the model R^2. This indicates that for BC the predictive ability of the developed models was underestimated by the model HV R squares. For UFP the agreement with the external dataset was larger than was predicted by the HV (24%). The models were spatially robust and well able to predict concentrations from previous studies. Possibly, the MUSiC study design in which the measurements at different site types were equally distributed over the sampling days attributed to decrease the influence of temporal variation.

The **advantage** of mobile sampling campaigns is that a large number of samples can be taken at many different locations efficiently. This allows for a better representation of different site types, increasing the accuracy of the models. In the MUSiC project for example, we were able to get 3 repeated samples at 161 sites in 7 months' time. In contrast, the ESCAPE study period lasted for around 12 months and measured PM pollutants at 20 (40 in the Netherlands) sites. Another advantage is that a field technician is always present during the sampling. The UFP monitoring equipment that was used in our study, the CPC3007, runs out of isopropanol after 6 hours and is therefore not a suitable instrument for long term monitoring. The CPC3022A, that was used in for example RUPIOH, is able to measure for longer sampling times. However this unit is much more expensive than the 3007 model. Leaving valuable equipment unattended at public spaces limits the locations where measurements can be

performed. In fixed sampling campaigns, the equipment is therefore often placed at the height of the first floor, on for example a balcony, to prevent vandalism. This illustrates another advantage for the mobile monitoring studies; measurements are always taken on ground level. Additionally, finding suitable sites is easier, since we measure at public spaces we don't need permission from residents or organizations to measure at their premises. Furthermore, in campaigns with fewer sampling sites, locations with complex configuration (such as intersections) are avoided, since these might be too difficult to be explained by the LUR models based upon a small number of sites. In mobile measurement campaigns this is less of a problem because of the large number of sites. Finally, an advantage of using continuous monitoring equipment is that directly usable results are obtained, without having to analyze samples in the lab.

A **disadvantage** of mobile sampling campaigns is the smaller sampling times compared to fixed sampling campaigns, which leads to a decrease in precision of the site-specific averages due to larger temporal variation. Table 4 shows an overview of mobile measurement campaigns that were conducted recently. Overall, the 15-60 minute measurements resulted in LUR models with an explained variability of 20-50% for the UFP concentrations.[46,48] These R^2 values are lower than reported for campaigns with longer sampling duration for the components NO_2, BC and $PM_{2.5.}$[23] The low precision of the site-specific averages likely contributes to these lower R^2 values. However, another reason for the lower model R^2 found for UFP might be that UFP is more difficult to model than NO_2, BC and $PM_{2.5.}$ In Amsterdam, model R^2 were indeed lower for UFP than for BC and $PM_{2.5}$.[51] In the New Delhi study, BC was modeled more effectively than UFP, though mostly with temporal predictors.[49] In the MUSiC campaign, we found little difference in model R^2 between UFP and BC. R^2 values of spatial and spatial-temporal models cannot be directly compared, as the spatial-temporal models contain both spatial and temporal predictors. In the New Delhi study, the temporal predictors contributed most to the model explained variance, with little contribution of the spatial predictors.[49] Another disadvantage of mobile campaigns is that continuous real-time sensors are required, which are not available for certain components (e.g. elemental composition of PM) or may be less reliable than the filter based methods (e.g. for $PM_{2.5}$). Given that technicians need to be present, it is more difficult to include nighttime and weekend periods. A study in Belgium suggested that LUR models for BC differed between weekends and weekdays and between daytime and nighttime.[37] For example, traffic variables were found to be more significant during daytime and were not included in the models during nighttime.

Some of the measurement campaigns presented in table 4 were based upon continuous mobile monitoring, without stopping at a certain number of sites.[45,47,50] These studies repeated their routes several times. This is

in contrast with our MUSiC campaign, where the actual measurements were stationary. It is unclear which of these designs is most efficient. For future mobile measuring studies, it seems advisable to sample more than 30 minutes per site or have more than 3 repeated measurements to reduce the effect of temporal spatial variation. An example of a sampling design, based on the MUSiC measurement schedule, is to take 2 repeated samples per season. Practically, the repeated sample could be taken in the 2 weeks following the original sample period for that season in that city.

In conclusion, for the development of LUR models a large contrast in spatial variation and therefore reducing the influence of temporal variation is important. The models that were developed using three repeated 30 minute samples seemed to deliver robust spatial predictor variables. However, it remains challenging to discriminate spatial variations from temporal variations. Model accuracy and precision could possibly improve with increased repeated sampling.

Conclusion

Exposure assessment for epidemiological studies of the effects of long-term exposure to air pollution on health remains challenging. LUR modelled $PM_{2.5}$ and NO_2 concentrations were not well correlated to personal exposure, probably mainly because of the influence of indoor sources and time activity patterns (time spent away from home). In contrast, modeled-personal soot did significantly correlate, probably because soot had fewer indoor sources. Epidemiological studies in the ESCAPE project did find health effects for LUR modelled $PM_{2.5}$. This can be explained by the finding that the $PM_{2.5}$ and NO_2 models were able to predict personal soot concentrations, the particle component with few indoor sources thus representing outdoor-derived particles. Adding variables for time activity, infiltration factors to the exposure models in addition to the LUR models could improve the predictions of personal exposure. Better separation of indoor and outdoor generated pollution could improve validation studies.
Air pollution consists of a complex mixture of components. The literature mostly describes models and health effects for NO_2 and $PM_{2.5}$. In this thesis, models were developed for the less well studied components UFP and BC. Our models explained 34-50% of the BC and 32-43% of the UFP spatial variability in concentrations. The models were able to significantly predict concentrations at completely independent sites from previous studies (R^2 61% for BC and 36% for UFP). Thus, despite the fairly low coefficients of determination, the models provided robust spatial predictions. This supports the use of short term or mobile measurement campaigns for the development of LUR models. Improving models for components which are less well evaluated, such as UFP models, could help to determine which air pollution components are mostly responsible for health effects.

Table 4 Comparison to other mobile/short term sampling campaigns.

Study	Location	Component	Nr of sites	Repeated samples	Sampling times	Model type	Overall R^2	Cross Validation	Median	Variability
Zwack, 2011[45]	Brooklyn, NY	UFP >6 nm ($10^3_* cm^{-3}$)	4 zones fixed walking routes	morning/ afternoon	2.5–3 hr	Sp-Temp	0.22-0.32	NA	40	SD: 24.8
Rivera, 2012[46]	Girona, Spain	UFP 20-100 nm ($10^3_* cm^{-3}$)	644	subset of 25 sites	15 min	Spatial	0.36	LOOCV: 0.35	8.3	Min – Max: 1.8 – 53
						Sp-Temp	0.51	LOOCV: 0.48		
Li, 2013[47]	Southern California	UFP 0−1000 nm ($10^3_* cm^{-3}$)	210 miles of roads	No	4-10 hours	Sp-Temp	0.45-0.55	LOOCV: 0.43-0.50	29	Min – Max: 16 – 110 IQR: 34
Abernethy, 2013[48]	Vancouver, Canada	UFP 10−1000 nm ($10^3_* cm^{-3}$)	80	No	60 minutes	Spatial	0.29−0.53	LOOCV: 0.36	14	SD: 16
Saraswat, 2013[49]	New Delhi, India	UFP 0−1000 nm ($10^3_* cm^{-3}$)	39	No	1−3 hours	Sp-Temp	0.23-0.28	LOOE: 0.71-0.59	40	IQR: 27-72
		BC (µg m^{-3})	26	No	1−3 hours	Sp-Temp	0.69-0.86	LOOE: 0.44-0.34	11	IQR: 6-21
Patton, 2014[50]	Somerville, MA	UFP >4 nm ($10^3_* cm^{-3}$)	fixed route	43 days	3-6 hours	Sp-Temp	0.38-0.53	NA	27	Min – Max: 2.7 – 1600 IQR: 43 SD :49
Montagne, 2014	Amsterdam/ Rotterdam, NL	UFP 10−1000 nm ($10^3_* cm^{-3}$)	161	3 seasons	30 minutes	Spatial	0.33-0.43	HV: 0.20-0.35	11	SD: 0.62
						Sp-Temp	0.32	HV: 0.18	11	SD: 0.72
		BC (µg m^{-3})	161	3 seasons	30 minutes	Spatial	0.35-0.41	HV: 0.15-0.29	1.17	SD: 0.73
						Sp-Temp	0.44	HV: 0.19	1.16	SD: 1.00

Sp-Temp= Spatial-Temporal, HV= hold-out validation, LOOCV= Leave One Out Cross Validation, LOOE= Leave One Out Evaluation, NA= Not Available, SD= Standard deviation

References

1. Janssen, N.A.H.; Lanki, T.; Hoek, G., et al Associations between ambient, personal, and indoor exposure to fine particulate matter constituents in Dutch and Finnish panels of cardiovascular patients. *Occup. Environ. Med.* **2005,** *62,* 868-877.

2. Ebelt, S.T.; Petkau, A.J.; Vedal, S.; Fisher, T.V.; Brauer, M. Exposure of chronic obstructive pulmonary disease patients to particulate matter: Relationships between personal and ambient air concentrations. *J. Air Waste Manage. Assoc.* **2000,** *50,* 1081-1094.

3. Delfino, R.J.; Staimer, N.; Gillen, D., et al Personal and ambient air pollution is associated with increased exhaled nitric oxide in children with asthma. *Environ. Health Perspect.* **2006,** *114,* 1736-1743.

4. Liu, L.; Ruddy, T.; Dalipaj, M., et al Effects of indoor, outdoor, and personal exposure to particulate air pollution on cardiovascular physiology and systemic mediators in seniors. *Journal of Occupational and Environmental Medicine* **2009,** *51,* 1088-1098.

5. Spira-Cohen, A.; Chen, L.C.; Kendall, M.; Lall, R.; Thurston, G.D. Personal exposures to traffic-related air pollution and acute respiratory health among bronx schoolchildren with asthma. *Environ. Health Perspect.* **2011,** *119,* 559-565.

6. Janssen, N.A.H.; De Hartog, J.J.; Hoek, G., et al Personal exposure to fine particulate matter in elderly subjects: Relation between personal, indoor, and outdoor concentrations. *Journal of the Air and Waste Management Association* **2000,** *50,* 1133-1143.

7. Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Temporal associations of ambient PM2.5 elemental concentrations with indoor and personal concentrations. *Atmos. Environ.* **2014,** *86,* 203-211.

8. Janssen, N.A.; Hoek, G.; Simic-Lawson, M., et al Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5. *Environ. Health Perspect.* **2011,** *119,* 1691-1699.

9. HEI Panel Traffic-related air pollution. A critical review of the literature on emissions, exposure and health effects. *Boston, MA: Health Effects Institute* **2010,** *Special Report 17,* Chapter 3.

10. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. *Atmospheric Environment* **2012,** *62,* 303-317.

11. Nethery, E.; Leckie, S.E.; Teschke, K.; Brauer, M. From measures to models: An evaluation of air pollution exposure assessment for epidemiological studies of pregnant women. *Occup. Environ. Med.* **2008,** *65,* 579-586.

12. Sahsuvaroglu, T.; Su, J.G.; Brook, J.; Burnett, R.; Loeb, M.; Jerrett, M. Predicting personal nitrogen dioxide exposure in an elderly population: Integrating residential indoor and outdoor measurements, fixed-site ambient pollution concentrations, modeled pollutant levels, and time-activity patterns. *J. Toxicol. Environ. Health Part A Curr. Iss.* **2009,** *72,* 1520-1533.

13. Diapouli, E.; Chaloulakou, A.; Koutrakis, P. Estimating the concentration of indoor particles of outdoor origin: A review. *J. Air Waste Manage. Assoc.* **2013,** *63,* 1113-1129.

14. Oglesby, L.; Kunzli, N.; Roosli, M., et al Validity of ambient levels of fine particles as surrogate for personal exposure to outdoor air pollution - Results of the European EXPOLIS-EAS study (Swiss Center Basel). *Journal of the Air and Waste Management Association* **2000,** *50,* 1251-1261.

15. Derudi, M.; Gelosa, S.; Sliepcevich, A., et al Emission of air pollutants from burning candles with different composition in indoor environments. *Environmental Science and Pollution Research* **2014,** *21,* 4320-4330.

16. Monn, C. Exposure assessment of air pollutants: a review on spatial heterogeneity and indoor/outdoor/personal exposure to suspended particulate matter, nitrogen dioxide and ozone. *Atmos. Environ.* **2001,** *35,* 1-32.

17. Wallace, L. Indoor Particles: A Review. *J. Air Waste Manage. Assoc.* **1996,** *46,* 98-126.

18. MacNeill, M.; Wallace, L.; Kearney, J., et al Factors influencing variability in the infiltration of PM2.5 mass and its components. *Atmos. Environ.* **2012,** *61,* 518-532.

19. Chen, C. and Zhao, B. Review of relationship between indoor and outdoor particles: I/O ratio, infiltration factor and penetration factor. *Atmos. Environ.* **2011,** *45,* 275-288.

20. Chen, Y.; Zheng, M.; Edgerton, E.S.; Ke, L.; Sheng, G.; Fu, J. PM 2.5 source apportionment in the southeastern U.S.: Spatial and seasonal variations during 2001-2005. *J. Geophys. Res. D Atmos.* **2012,** *117,* D08304.

21. Clougherty, J.E.; Houseman, E.A.; Levy, J.I. Source apportionment of indoor residential fine particulate matter using land use regression and constrained factor analysis. *Indoor Air* **2011,** *21,* 53-66.

22. Levy, J.I.; Clougherty, J.E.; Baxter, L.K.; Houseman, E.A.; Paciorek, C.J.; HEI Health Review Committee Evaluating heterogeneity in indoor and outdoor air pollution using land-use regression and constrained factor analysis. *Res. Rep. Health Eff. Inst.* **2010,** 5-80; discussion 81-8091.

23. Hoek, G.; Beelen, R.; de Hoogh, K., et al A review of land-use regression models to assess spatial variation of outdoor air pollution. *Atmos. Environ.* **2008,** *42,* 7561-7578.

24. Wang, M.; Beelen, R.; Basagana, X., et al Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project. *Environ. Sci. Technol.* **2013,** *47,* 4357-4364.

25. De Hoogh, K.; Wang, M.; Adam, M., et al Development of land use regression models for particle composition in twenty study areas in Europe. *Environ. Sci. Technol.* **2013,** *47,* 5778-5786.

26. Sarnat, S.E.; Coull, B.A.; Ruiz, P.A.; Koutrakis, P.; Suh, H.H. The influences of ambient particle composition and size on particle infiltration in Los Angeles, CA, residences. *J. Air Waste Manag. Assoc.* **2006,** *56,* 186-196.

27. Abt, E.; Suh, H.H.; Catalano, P.; Koutrakis, P. Relative Contribution of Outdoor and

Indoor Particle Sources to Indoor Concentrations. *Environ. Sci. Technol.* **2000,** *34,* 3579-3587.

28. Long, C.M.; Suh, H.H.; Catalano, P.J.; Koutrakis, P. Using time- and size-resolved particulate data to quantify indoor penetration and deposition behavior. *Environ. Sci. Technol.* **2001,** *35,* 2089-2099.

29. Hoek, G.; Kos, G.; Harrison, R., et al Indoor-outdoor relationships of particle number and mass in four European cities. *Atmos. Environ.* **2008,** *42,* 156-169.

30. Lianou, M.; Chalbot, M.-.; Kotronarou, A., et al Dependence of home outdoor particulate mass and number concentrations on residential and traffic features in urban areas. *Journal of the Air and Waste Management Association* **2007,** *57,* 1507-1517.

31. Dons, E.; Int Panis, L.; Van Poppel, M., et al Impact of time-activity patterns on personal exposure to black carbon. *Atmos. Environ.* **2011,** *45,* 3594–3602.

32. Setton, E.; Marshall, J.D.; Brauer, M., et al The impact of daily mobility on exposure to traffic-related air pollution and health effect estimates. *J. Expo. Sci. Environ. Epidemiol.* **2011,** *21,* 42-48.

33. Lanki, T.; Ahokas, A.; Alm, S., et al Determinants of personal and indoor PM2.5 and absorbance among elderly subjects with coronary heart disease. *Journal of Exposure Science and Environmental Epidemiology* **2007,** *17,* 124-133.

34. Van Roosbroeck, S.; Hoek, G.; Meliefste, K.; Janssen, N.A.H.; Brunekreef, B. Validity of residential traffic intensity as an estimate of long-term personal exposure to traffic-related air pollution among adults. *Environmental Science and Technology* **2008,** *42,* 1337-1344.

35. Brunekreef, B.; Janssen, N.A.; de Hartog, J.J., et al Personal, indoor, and outdoor exposures to PM2.5 and its components for groups of cardiovascular patients in Amsterdam and Helsinki. *Res. Rep. Health Eff. Inst.* **2005,** 1-70; discussion 71-79.

36. Dons, E.; Van Poppel, M.; Kochan, B.; Wets, G.; Int Panis, L. Implementation and validation of a modeling framework to assess personal exposure to black carbon. *Environ. Int.* **2014,** *62,* 64-71.

37. Dons, E.; Van Poppel, M.; Kochan, B.; Wets, G.; Int Panis, L. Modeling temporal and spatial variability of traffic-related air pollution: Hourly land use regression models for black carbon. *Atmos. Environ.* **2013,** *74,* 237-246.

38. De Nazelle, A.; Seto, E.; Donaire-Gonzalez, D., et al Improving estimates of air pollution exposure through ubiquitous sensing technologies. *Environmental Pollution* **2013,** *176,* 92-99.

39. Beelen, R.; Stafoggia, M.; Raaschou-Nielsen, O., et al Long-term exposure to air pollution and cardiovascular mortality: An analysis of 22 European cohorts. *Epidemiology* **2014,** *25,* 368-78.

40. Raaschou-Nielsen, O.; Andersen, Z.J.; Beelen, R., et al Air pollution and lung cancer incidence in 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE). *Lancet Oncol.* **2013,** *14,* 813-22.

41. Dimakopoulou, K.; Samoli, E.; Beelen, R., et al Air pollution and nonmalignant respiratory mortality in 16 cohorts within the ESCAPE project. *American Journal of Respiratory and Critical Care Medicine* **2014,** *189,* 684-696.

42. Kelly, F.J. and Fussell, J.C. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmos. Environ.* **2012,** *60,* 504-526.

43. Wang, M.; Beelen, R.; Stafoggia, M., et al Long-term exposure to elemental constituents of particulate matter and cardiovascular mortality in 19 European cohorts: Results from the ESCAPE and TRANSPHORM projects. *Environ. Int.* **2014,** *66,* 97-106.

44. Armstrong, B.G. Effect of measurement error on epidemiological studies of environmental and occupational exposures. *Occup. Environ. Med.* **1998,** *55,* 651-656.

45. Zwack, L.M.; Paciorek, C.J.; Spengler, J.D.; Levy, J.I. Characterizing local traffic contributions to particulate air pollution in street canyons using mobile monitoring techniques. *Atmos. Environ.* **2011,** *45,* 2507-2514.

46. Rivera, M.; Basagaña, X.; Aguilera, I., et al Spatial distribution of ultrafine particles in urban settings: A land use regression model. *Atmos. Environ.* **2012,** *54,* 657-666.

47. Li, L.; Wu, J.; Hudda, N.; Sioutas, C.; Fruin, S.A.; Delfino, R.J. Modeling the concentrations of on-road air pollutants in Southern California. *Environmental Science and Technology* **2013,** *47,* 9291-9299.

48. Abernethy, R.C.; Allen, R.W.; McKendry, I.G.; Brauer, M. A Land Use Regression Model for Ultrafine Particles in Vancouver, Canada. *Environ. Sci. Technol.* **2013,** *47,* 5217–5225.

49. Saraswat, A.; Apte, J.S.; Kandlikar, M.; Brauer, M.; Henderson, S.B.; Marshall, J.D. Spatiotemporal land use regression models of fine, ultrafine, and black carbon particulate matter in New Delhi, India. *Environmental Science and Technology* **2013,** *47,* 12903-12911.

50. Patton, A.P.; Collins, C.; Naumova, E.N.; Zamore, W.; Brugge, D.; Durant, J.L. An hourly regression model for ultrafine particles in a near-highway urban area. *Environmental Science and Technology* **2014,** *48,* 3272-3280.

51. Hoek, G.; Beelen, R.; Kos, G., et al Land use regression model for ultrafine particles in Amsterdam. *Environ. Sci. Technol.* **2011,** *45,* 622-628.

52. Fuller, C.H.; Brugge, D.; Williams, P.L.; Mittleman, M.A.; Durant, J.L.; Spengler, J.D. Estimation of ultrafine particle concentrations at near-highway residences using data from local and central monitors. *Atmos. Environ.* **2012,** *57,* 257-265.

53. Wang, M.; Beelen, R.; Eeftens, M.; Meliefste, K.; Hoek, G.; Brunekreef, B. Systematic evaluation of land use regression models for NO 2. *Environ. Sci. Technol.* **2012,** *46,* 4481-4489.

54. Basagaña, X.; Rivera, M.; Aguilera, I., et al Effect of the number of measurement sites on land use regression models in estimating local air pollution. *Atmos. Environ.* **2012,** *54,* 634-642.

Summary

Summary

Many studies have found an association between air pollution and health effects. Less is known about which components of air pollution are responsible. To be able to study the health effects of different components of air pollution in large groups of people, epidemiological studies are conducted. For these studies, assessing exposure accurately for the study participants is important. Land use regression (LUR) models are often used to predict the outdoor air pollution at the home address of study participants, to study long-term effects of air pollution. While several studies have documented that $PM_{2.5}$ mass measured at a central site correlates well in **time** with personal exposure, little is known about how well **spatial** variation of home outdoor concentration predictions represent personal exposure. People spent most of their time indoors and long hours at work, at school or in other micro environments. Furthermore little is known about how well temporal variation of the elemental composition of $PM_{2.5}$ at a central site is correlated with personal exposure. Many time series studies use central site measurements as a proxy for personal exposure. Currently, LUR models have been developed extensively for NO_2 and $PM_{2.5}$, but not for ultrafine particles (UFP). Data on the long-term health effects of UFP is limited by lack of adequate models. Recently mobile monitoring has been explored to develop LUR models for UFP.

The **aims** of this thesis were:

1. To assess the association between LUR predicted home outdoor concentrations and measured personal exposure of particulate matter with a diameter of <2.5 μm ($PM_{2.5}$), soot, NO_2, NO_x and the elemental composition of $PM_{2.5}$. The elements of interest were Cu, Zn, Fe, K, Ni, V, Si and S.
2. To assess the temporal association of $PM_{2.5}$ elemental composition measured at a central site with measured personal exposure
3. To develop LUR models for UFP and BC using a mobile monitoring campaign.

The first two aims were addressed by setting up the VE^{3}SPA study (Validation of ESCAPE Exposure EstimateS using Personal exposure Assessment). Outdoor and indoor concentrations were measured at 15 participants in Utrecht (the Netherlands), Helsinki (Finland) and Barcelona (Spain). Simultaneously, the personal exposure was measured for these 45 participants. LUR models predict annual averages of air pollution, so for an equal comparison we tried to diminish the influence of temporal variation for the personal exposure measurements by performing repeated sampling. Measurements were conducted for 6 times 96 hours (Monday-Friday) in three different seasons (winter, summer and spring/autumn). The spatial correlation of the LUR models with the outdoor/indoor/personal measured concentrations was determined with regression analyses.

Soot LUR models were significantly correlated with measured average outdoor and personal soot concentrations (Chapter 2). Soot LUR models explained 39%, 44% and 20% of personal exposure variability (R^2) in Helsinki, Utrecht and Barcelona. NO_2 LUR models significantly predicted outdoor concentrations and personal exposure in Utrecht and Helsinki. $PM_{2.5}$ models were moderately correlated to the outdoor concentrations in Utrecht and Helsinki, but not in Barcelona. No correlations were found between LUR modeled and personal $PM_{2.5}$ in any of three cities. Significant associations were found between LUR modeled and personal $PM_{2.5}$, NO_2 and soot when data from the cities were pooled.

LUR models predicted the within-city variation of average outdoor Cu and Fe concentrations moderately well (Chapter 3). The range in R^2 was 27-67% for Cu and 24-54% for Fe. The outdoor concentrations of K, Ni, S, Si, V and Zn were not well predicted. The LUR modeled concentration correlated significantly with measured personal Fe exposure in Utrecht and Ni and V in Helsinki only. The LUR model predictions did not correlate with measured personal Cu exposure. Overall, the within-city modeled variation of the elemental composition of $PM_{2.5}$ did not predict the measured variation in personal exposure well.

In chapter 4, the temporal associations of $PM_{2.5}$ elemental composition measured at a central site with the personal measurements were determined. The within-person correlations of the 6 outdoor/indoor/personal measurements with the corresponding central site measurements were determined. The median correlation per city was determined of the 15 within-person correlations. The temporal variation at a central site was highly correlated with personal exposure for Fe, K, Ni, S, Si, V and Zn, but not for Cu. The highest correlations (Pearson's R) were found for S and V (R above 0.85). Lower correlations were found for the elements Cu, Fe and Si associated with non-tailpipe traffic emissions and road dust. For $PM_{2.5}$ mass the R was lower (between 0.37 and 0.70). The generally high correlation between temporal variation of the outdoor concentration and personal exposure supports the use of a central site for assessing exposure of PM components in time series studies for most elements.

The third aim was addressed by setting up the MUSiC study (Measurements of Ultrafine particles and Soot in Cities). The MUSiC project was a short-term (mobile) measurement campaign in which measurements were done for 30 minutes at 80/81 sites in Rotterdam and Amsterdam (the Netherlands), respectively. Measurements were repeated in three seasons. LUR models for UFP and BC were developed using the GIS predictors and methodology from the ESCAPE study (European Study of Cohorts for Air Pollution Effects).

In chapter 5 we determined the within site temporal and between site spatial variation to assess spatial variation of UFP and BC with short term samples. The within-sites variance was 2.21 and 3.25 times higher than the between-sites variance for UFP and BC, respectively. These ratios were substantially higher than for studies with longer sampling durations. Average street to urban background ratios were similar for UFP and BC (1.5 and 1.6 respectively).

In chapter 6 the UFP and BC LUR models based upon short-term monitoring are presented. Models were developed for Amsterdam and Rotterdam separately and for the two cities pooled; using only spatial (GIS predictors) data or including temporal data (e.g. weather conditions). The percentage explained variability (R^2) varied between 0.34-0.50 for BC and 0.32-0.43 for UFP. Traffic variables were present in every model. The LUR models for UFP and especially BC predicted spatial contrasts from external datasets, derived from previous campaigns based on longer sampling durations, well. This supports further development of these short-term measurement campaigns to develop spatial LUR models.

In conclusion, predicting the exposure of study participants for epidemiological studies remains challenging. LUR models were better able to predict the personal exposure for components with fewer indoor sources, such as soot. The short-term sampling campaign for UFP and BC delivered fairy robust models. Improving models for components which are less well evaluated in the literature, such as UFP models, could help to determine which air pollution components are mostly responsible for the health effects.

Samenvatting

Samenvatting

Vele studies hebben aangetoond dat luchtvervuiling effect kan hebben op de volksgezondheid. Welke luchtvervuilingscomponenten precies verantwoordelijk hiervoor zijn is minder bekend. Het meest onderzochte component is fijnstof. Fijnstof wordt ook wel $PM_{2.5}$ genoemd omdat het hier gaat om deeltjes met een diameter kleiner dan 2.5 micrometer. Dit is relevant voor de gezondheid omdat het de longen kan binnendringen. Fijnstof is opgebouwd uit verschillende componenten, waaronder roet. Verder komt er bij verbranding van brandstof stikstofoxide (NO) vrij, dat bij contact met de buitenlucht wordt omgezet in NO_2. NO_2 wordt daarom vaak gebruikt als een indicator voor verkeers-gerelateerde luchtvervuiling. Om uit te zoeken wat de gezondheidseffecten van alle verschillende componenten zijn voor grote groepen mensen worden epidemiologische studies uitgevoerd. Voor deze studies is een accurate inschatting van de blootstelling belangrijk. Met regelmaat worden zogenaamde "land use regression (LUR)" modellen ingezet om de buitenluchtconcentraties bij studie deelnemers thuis te voorspellen. Voor deze modellen worden geografische informatie systemen (GIS) gebruikt. Deze systemen bevatten bijvoorbeeld informatie over verkeersaantallen en groenvoorzieningen in verschillende bufferzones (bijvoorbeeld 50, 100 of 200 meter) van het beoogde studie adres.

Verschillende studies hebben aangetoond dat de variaties in $PM_{2.5}$ massa op een centraal meetpunt **in de tijd** goed correleert met persoonlijke blootstellingsconcentraties. Echter, er is minder bekend over hoe goed de **ruimtelijke** verschillen in buitenluchtconcentraties op verschillende adressen correleert met de persoonlijke blootstelling van de mensen die op deze adressen wonen. Mensen zijn niet alleen maar blootgesteld aan de buitenluchtkwaliteit rondom hun huis. De meeste tijd besteden ze in huis en verder gaan ze naar hun werk, school of andere omgevingen.

Er worden veel tijd-series studies uitgevoerd waarvoor metingen op een centraal punt in een stad worden gebruikt als benadering van de persoonlijke blootstellingsvariaties in de tijd. Toch is weinig bekend over hoe goed de variaties van elementaire componenten van $PM_{2.5}$ in de tijd op een centraal meetpunt overeenkomt met variaties in persoonlijke blootstelling.

Momenteel zijn vooral veel LUR modellen ontwikkeld voor NO_2, $PM_{2.5}$ en black carbon (BC), een onderdeel van roet. Voor ultra-fijnstof (UFP), deeltjes met een diameter kleiner dan 100 nanometer, zijn echter nog maar weinig LUR modellen ontwikkeld. Er is mede hierdoor ook nog niet veel bekend over de lange termijn gezondheidseffecten van UFP. Recentelijk is wel een aantal mobiele meetcampagnes opgezet om UFP te meten en LUR modellen te maken.

De doelen van dit proefschrift zijn:

1. Het bepalen van de associaties tussen de door LUR modellen voorspelde buitenluchtconcentraties en de gemeten persoonlijke blootstelling. De onderzochte componenten waren $PM_{2.5}$, roet, NO_2, NO_x en elementaire componenten in $PM_{2.5.}$ De onderzochte componenten waren koper (Cu), Zink (Zn), ijzer (Fe), kalium (K), nikkel (Ni), vanadium (V), silicium (Si) en zwavel (S).
2. De associatie *in de tijd* van de elementaire componenten van $PM_{2.5}$ gemeten op een centraal punt met de persoonlijke blootstelling.
3. Het ontwikkelen van LUR modellen voor ultra-fijnstof (UFP) en black carbon (BC) met een mobiele meetcampagne waarin korte termijn metingen worden gedaan.

De eerste twee doelen werden onderzocht door de zogenaamde VE^3SPA (validatie van blootstellingsschattingen met behulp van persoonlijke blootstellingsbepalingen) studie op te zetten. De LUR modellen zijn ontwikkeld door het ESCAPE project, een groot Europees project waar instituten uit 16 landen aan meededen. Voor de VE^3SPA studie werden buiten- en binnenlucht concentraties gemeten bij 15 deelnemers uit Utrecht (Nederland), Helsinki (Finland) en Barcelona (Spanje). Tegelijkertijd werd de persoonlijke blootstelling gemeten bij deze 45 vrijwilligers met behulp van meetpompen die in rugzakjes werden meegedragen. De LUR modellen voorspellen gemiddelde jaarlijkse concentraties, maar het is onpraktisch om de persoonlijke blootstelling gedurende een jaar te meten. Om de concentraties goed te kunnen vergelijken werd daarom in 3 seizoenen (winter, zomer en herfst/lente) gemeten en werden correcties gedaan voor verschillen in de tijd. In totaal werd er 6 keer gedurende 96 uur (van maandag t/m vrijdag) gemeten. De ruimtelijke correlaties tussen de gemodelleerde en de buiten/binnen/persoonlijke gemeten concentraties werden bepaald met behulp van regressieanalyses.

De LUR modellen voor roet waren significant gecorreleerd met de gemeten buitenlucht en met de persoonlijke roet concentraties (Hoofdstuk 2). De roet modellen verklaarden respectievelijk 39%, 44% en 20% van de persoonlijke blootstelling in Helsinki, Utrecht en Barcelona. De NO_2 LUR modellen voorspelden de buitenluchtconcentraties in Utrecht en Helsinki. De $PM_{2.5}$ modellen waren in staat om de buitenluchtconcentraties in Utrecht en Helsinki, maar niet Barcelona, te voorspellen. De modellen correleerden niet met de persoonlijke $PM_{2.5}$ en NO_2 concentraties.

De LUR modellen voor Cu en Fe waren redelijk in staat om de binnen-stads variatie in concentraties te voorspellen (Hoofdstuk 3). De determinatie coëfficiënt (R^2) waarden zaten tussen de 27-67% voor koper en 24-54% voor ijzer. De modellen waren niet in staat om de buitenluchtconcentraties

voor K, Ni, S, Si, V en Zn te voorspellen. De LUR modellen correleerden slechts met de persoonlijke concentraties voor Fe in Utrecht en Ni en V in Helsinki. De persoonlijke Cu concentraties waren niet gecorreleerd. Samengevat kwamen de binnen-stads gemodelleerde variatie voor de elementaire componenten in $PM_{2.5}$ niet goed overeen met de variatie in persoonlijke blootstelling.

In hoofdstuk 4 werden de associaties van variaties in de tijd van $PM_{2.5}$ elementaire componenten, gemeten op een centraal punt in een stad, met persoonlijk gemeten concentraties bepaald. De binnen-persoon correlaties van de zes 96-uurs buiten/binnen/persoonlijke metingen met de tegelijkertijd gemeten concentraties op het centrale punt werden bepaald. Daarna werd de mediaan correlatie van de 15 deelnemers per stad bepaald. De variatie in de tijd op een centraal meetpunt had een hoge correlatie met persoonlijke blootstelling voor Fe, K, Ni, S, Si, V en Zn, maar niet voor Cu. De grootste correlatie (Pearson's R) werd gevonden voor S en V (R tussen 0.87 en 0.98). Lagere correlaties werden gevonden voor de elementen die geassocieerd worden met niet-uitlaat gerelateerde verkeersuitstoot en opwervelend stof, namelijk Cu, Fe en Si (R tussen -0.34 en 0.79). De correlatie voor $PM_{2.5}$ massa was lager, namelijk 0.37-0.70. De over het algemeen hoge correlaties voor variaties in de tijd gemeten op een centraal punt en persoonlijke blootstelling ondersteunt het gebruik van een centraal meetpunt voor tijd-series studies voor de meeste van de hier onderzochte elementen.

Met behulp van het MUSiC (metingen van ultrafijnstof en roet in 2 steden) project werden LUR modellen voor UFP en BC ontwikkeld. Er werden korte termijns-metingen gedaan met behulp van een mobiel meetstation. In totaal werd op 80 plekken in Rotterdam en 81 in Amsterdam gemeten gedurende 30 minuten. De metingen werden in 3 verschillende seizoenen herhaald. De gemeten UFP en BC concentraties werden gebruikt om LUR modellen te ontwikkelen volgens de ESCAPE methode met behulp van GIS variabelen. In het vijfde hoofdstuk werd de precisie van bepalingen van ruimtelijke concentratie variaties op basis van korte termijn metingen ingeschat. De precisie van de schattingen voor de lange-termijn gemiddelde concentraties was laag. De binnen-locatie variaties waren 2.21 (voor UFP) en 3.25 (voor BC) keer hoger dan de tussen-locatie variaties. Deze ratio's waren substantieel hoger dan voor studies met langere meettijden.

In hoofdstuk 6 worden de UFP en BC modellen gepresenteerd. De modellen werden voor Amsterdam en Rotterdam apart en voor de twee steden samen ontwikkeld. Voor de modellen werden ruimtelijke (GIS) en temporele variabelen (weersomstandigheden) gebruikt. De modellen werden vervolgens toegepast om concentraties te voorspellen op locaties waar in eerdere studies de concentraties waren gemeten met langere meettijden. De LUR modellen waren redelijk in staat om de ruimtelijke contrasten in

deze externe datasets te voorspellen. Deze bevindingen ondersteunen het gebruik van korte termijns-metingen voor de ontwikkeling van LUR modellen.

Ter conclusie, het voorspellen van de blootstelling voor deelnemers in een epidemiologische studie blijft een uitdaging. De LUR modellen waren beter in staat om de persoonlijke blootstelling voor componenten met minder binnenlucht bronnen, zoals roet, te voorspellen. De korte termijns-metingen van het MUSiC project leverde redelijk robuuste modellen op. Het verbeteren van modellen voor componenten die minder goed worden beschreven in de literatuur, zoals UFP, kunnen helpen om te bepalen welke componenten in luchtvervuiling vooral verantwoordelijk zijn voor de gezondheidseffecten.

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Curriculum Vitae

Denise Rolinka Montagne was born on February 23 1985 in Leiden, the Netherlands and grew up in Oegstgeest. After graduating from high school (Visser 't Hooft Lyceum, Leiden) in 2003 she studied Biomedical Sciences at the University of Utrecht. She completed her bachelor in 2007 and started her Master Biology of Disease at Utrecht University. Her 6 month internship was at the department of Medical Physiology of the University Medical Centre Utrecht (UMCU), where she studied the canine KCNJ2 gene structure. She did her 9-month research training at the Institute of Risk Assessment Sciences (IRAS, Utrecht University), studying air quality at three locations in Utrecht and the effect on exhaled NO. In 2009 she obtained her Master's degree and started working as a PhD student at the Environmental Epidemiology (EEPI) department of IRAS. The results of her PhD study are described in this thesis. In June 2014 she started working at QPS, a clinical research organisation (CRO) in Groningen, the Netherlands.

List of publications

Yang, A.; Hoek, G.; Montagne, D.; Brunekreef, B.; Leseman, D.; Hellack, B.; Kuhlbusch, T.; Cassee, F.; Janssen, N. Agreement of central site measurements and land use regression modeled oxidative potential of PM2.5 with personal exposure, *Submitted*

Montagne, D.R.; Hoek, G.; Klompmaker, J.O.; Wang, M.; Meliefste, K.; Brunekreef, B. Land use regression models for ultrafine particles and black carbon based on short-term monitoring predict past spatial variation. *Submitted*

Klompmaker, J.O.; Montagne, D.R.; Meliefste, K.; Hoek, G.; Brunekreef, B. Spatial variation of ultrafine particles and black carbon in two cities: Results from a short-term measurement campaign. *Sci. Total Environ.* **2014,** *508C,* 266-275.

Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Temporal associations of ambient PM2.5 elemental concentrations with indoor and personal concentrations. *Atmos. Environ.* **2014,** *86,* 203-211.

Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al The association of LUR modeled PM2.5 elemental composition with personal exposure. *Sci. Total Environ.* **2014,** *493,* 298-306.

Montagne, D.; Hoek, G.; Nieuwenhuijsen, M., et al Agreement of land use regression models with personal exposure measurements of particulate matter and nitrogen oxides air pollution. *Environ. Sci. Technol.* **2013,** *47,* 8523-8531.

Boogaard, H.; Montagne, D.R.; Brandenburg, A.P.; Meliefste, K.; Hoek, G. Comparison of short-term exposure to particle number, PM10 and soot concentrations on three (sub) urban locations. *Sci. Total Environ.* **2010,** *408,* 4403-4411.

Houtman, M.J.; Takanari, H.; Kok, B.G.; van Eck, M.; Montagne, D.R.; Vos, M.A.; de Boer, T.P.; van der Heyden, M.A. Experimental Mapping of the Canine KCNJ2 and KCNJ12 Gene Structures and Functional Analysis of the Canine K(IR)2.2 ion Channel. *Front. Physiol.* **2012,** *3*, 9.

Dunnink, A.; Sharif, S.; Oosterhoff, P.; Winckels, S.; Montagne, D.; Beekman, J.; van der Nagel, R.; van der Heyden, M.A.; Vos, M.A. Anesthesia and arrhythmogenesis in the chronic atrioventricular block dog model. *J. Cardiovasc. Pharmacol.* **2010,** *55* (6), 601-608.

Dankwoord

Dankwoord

Het is gelukt, het boekje is klaar! Hier voor je ligt het resultaat van 4,5 jaar werk. Maar ik heb het natuurlijk niet alleen gedaan. Het PhD traject was voor mij een mooie tijd, waarin ik veel heb geleerd en inspirerende mensen heb ontmoet.

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De meetapparatuur/ The equipment

VE³SPA

Buitenluchtpomp/ Outdoor unit

Het rugzakje/ The backpack

MUSiC

De "tank"

De fietskar/ The bike trailer