Modeling of residential outdoor exposure to traffic air pollution and assessment of associated health effects

INAUGURALDISSERTATION

zur

Erlangung der Würde einer Doktorin der Philosophie
vorgelegt der
Philosophisch-Naturwissenschaftlichen Fakultät
der Universität Basel

von

Regina Elisabeth Ducret-Stich
aus Kleinlützel (SO) und Plan-les-Ouates (GE)

Basel, 2014

Namensnennung-Keine kommerzielle Nutzung-Keine Bearbeitung 3.0 Schweiz
(CC BY-NC-ND 3.0 CH)

Sie dürfen: **Teilen** — den Inhalt kopieren, verbreiten und zugänglich machen

Unter den folgenden Bedingungen:

Namensnennung — Sie müssen den Namen des Autors/Rechteinhabers in der von ihm festgelegten Weise nennen.

Keine kommerzielle Nutzung — Sie dürfen diesen Inhalt nicht für kommerzielle Zwecke nutzen.

Keine Bearbeitung erlaubt — Sie dürfen diesen Inhalt nicht bearbeiten, abwandeln oder in anderer Weise verändern.

Wobei gilt:

- **Verzichtserklärung —** Jede der vorgenannten Bedingungen kann **aufgehoben** werden, sofern Sie die ausdrückliche Einwilligung des Rechteinhabers dazu erhalten.
- **Public Domain (gemeinfreie oder nicht-schützbare Inhalte) —** Soweit das Werk, der Inhalt oder irgendein Teil davon zur Public Domain der jeweiligen Rechtsordnung gehört, wird dieser Status von der Lizenz in keiner Weise berührt.
- **Sonstige Rechte —** Die Lizenz hat keinerlei Einfluss auf die folgenden Rechte:
    - Die Rechte, die jedermann wegen der Schranken des Urheberrechts oder aufgrund gesetzlicher Erlaubnisse zustehen (in einigen Ländern als grundsätzliche Doktrin des **fair use** bekannt);
    - Die **Persönlichkeitsrechte** des Urhebers;
    - Rechte anderer Personen, entweder am Lizenzgegenstand selber oder bezüglich seiner Verwendung, zum Beispiel für **Werbung** oder Privatsphärenschutz.
- **Hinweis —** Bei jeder Nutzung oder Verbreitung müssen Sie anderen alle Lizenzbedingungen mitteilen, die für diesen Inhalt gelten. Am einfachsten ist es, an entsprechender Stelle einen Link auf diese Seite einzubinden.

Quelle: http://creativecommons.org/licenses/by-nc-nd/3.0/ch/ Datum: 12.11.2013

Genehmigt von der Philosophisch-Naturwissenschaftlichen Fakultät

auf Antrag von

Prof. Dr. Marcel Tanner

Prof. Dr. med. Nino Künzli

Prof. Dr. Eberhard Parlow

Basel, den 11. Dezember 2012

Prof. Dr. Jörg Schibler

Dekan der Philosophisch-Naturwissenschaftlichen Fakultät

Not everything that counts can be counted,
and not everything that can be counted counts.

William Bruce Cameron

Table of contents

Acknowledgements

This thesis was carried out within the framework of two studies: the Southern California study, supported by the National Institute of Environmental Health Sciences (ES11615) of the U.S. National Institutes of Health (NIH); and the MfM-U (Monitoring flankierende Massnahmen – Umwelt) study, funded by the Federal Office for the Environment FOEN (No. 050303 /516 G161-1955) of the Swiss Government. The work was carried out at the Institute of Social and Preventive Medicine of the University of Basel, Switzerland, and at the Swiss Tropical and Public Health Institute in Basel. Switzerland.

I would like to dedicate this thesis to my former supervisor, Prof. Jane-Lee Sally Liu, who passed away in June 2011. First of all she gave me the opportunity to drive my career into a new direction. She was always supportive in the supervision of my work and never short of new ideas. Even during her illness she stayed optimistic and enthusiastic. Thanks to her flexibility, I was able to combine family responsibilities and work. I am deeply grateful for her guidance throughout this work and will keep her in good memories.

I would like to thank the many persons who contributed in different ways to this work. Very special thanks go to Harish Phuleria, who was always there when I needed help with my work. He helped and supported me in the difficult times, when Sally was not available. I am very grateful for his encouragement and patience at all times. We had many interesting discussions and had always a helping hand in difficult times.

I would also thank the team under Prof. Ralph Delfino from the University of California in Irvine, namely Thomas Tjoa and June Wu. They patiently answered all my questions to the data set provided for my work. I am also grateful for all the help of Ralph Delfino in writing up the journal paper.

Many thanks go to the participating children in the MfM-U study and their parents in Erstfeld. They showed great power of endurance by coming month for month to the health monitoring. They also patiently endured our air pollution measurements at their homes.

Special thanks go to the exposure group team at the Swiss TPH. Special thank go to Alex Ineichen, who organized and accompanied me to all the fieldwork trips. Thanks go also to Martina Ragettli, who always was there when somebody was needed for fieldwork. I would like to thank also Ming Tsai for his support and Harish Phuleria for his constant inputs and supervision.

I would also like to thank the inNet team, namely Peter Böhler and Raffael Känzig, for collecting and providing all the air pollution measurements and meteorological data.

Thanks go also to Dr. Jürg Hammer and Dr. Dominik Müller from the University Childrens Hospital in Basel. They allowed us to use their equipment for analyzing the collected breath samples. They also provided and carried out the skin prick tests.

I would also like to thank Dr. Roger Lauener and especially Susanne Löliger from the University Childrens Hospital in Zürich. They provided and carried out the analysis of the collected breath condensates.

I also would like to thank Mark Davy from the University of Washington in Seattle for his input and help with the technical issues of the home air pollution measurements.

I am also grateful to Prof. Phil Hopke for his numerous inputs and help with the source apportionment analysis. I appreciated his willingness to come to Basel to give a special source apportionment workshop for our group.

Many thanks go to PD. Christian Schindler, who spent hours with me to help with the statistical analyses. We always had long and fruitful discussions.

I would also like to thank Prof. Nino Künzli, who readily took over as supervisor of my thesis after Sally Liu passed away. With his great experience in the field of epidemiology, he always gave great inputs to my work.

Thanks go also to Prof. Charlotte Braun-Fahrländer, who often helped me with issues concerning the health analysis and serves as an expert in my thesis committee.

I would also like to thank Prof. Eberhard Parlow for assuming the co-reference of my thesis, and Prof. Marcel Tanner for accepting the function of representative of the Faculty of Science.

I wish to thank Martina Ragettli, Christian Schindler, Axel Ducret and Claude Ducret for proofreading parts of my thesis and giving me helpful feedback.

Finally I would like to thank my family for always supporting me. Special thanks go to my children Yannick and Myriam Ducret, who often had to take over the household chores, when I was too busy.

Summary

Background

Air pollution is known to affect cardiopulmonary health in the population. Traffic-related air pollution is of special interest, as increasing urbanization forces the people to live closer to busy roads. Children with asthma are amongst the most susceptible groups. Several epidemiological studies linked traffic air pollution with increased reporting of asthmatic symptoms and decreased lung function. New approaches with pulmonary inflammation biomarkers allow assessment of acute effects induced by air pollution.

Populations are usually not exposed to one but rather to a mixture of pollutants emitted by various sources. In addition, classical epidemiological studies, typically using air pollution levels measured at one central site, were not able to capture different spatiotemporal distributions of the pollutants. Therefore different modeling approaches are in use to refine the spatiotemporal component as well as the source component in exposure assessment.

Objectives

The aims of this thesis are (1) to build models for estimating short-term residential outdoor exposure to traffic-related air pollution, (2) to find and apportion source contributions to PM_{10} and (3) to examine the relationship between spatially refined exposure estimates and respiratory health effects in children with asthma.

Methods

This thesis was conducted within the framework of two pediatric asthma panel studies: a Southern California study in the greater Los Angeles area, and the MfM-U (Monitoring flankierende Massnahmen – Umwelt) study in a Swiss Alpine valley.

In the Southern California study continuous measurements of personal air pollution exposure were collected in 63 children living in Riverside, a smog

receptor site downwind from Los Angeles, and Whittier, a site immediately downwind of vehicular emission sources. Eight 10-day monitoring periods of personal particulate matter ≤ 2.5µm ($PM_{2.5}$), elemental carbon (EC), and organic carbon (OC) measurements each were conducted in Riverside from August to December 2003 and in Whittier from July to November 2004. During the same monitoring periods, one home site and a fixed central site were monitored concurrently. Local traffic-related air pollution contributions at each participants home were estimated with the CALINE4 dispersion. The home site measurements were then used to build models for estimating $PM_{2.5}$, EC, and OC concentrations at all other participating children's homes. To build the models we used land-use regression methods including fixed site measurements as additional temporal varialble and the CALINE4 estimates as additional spatial variable. We analyzed city-specific and pooled models and compared the home outdoor estimates with the personal measurements.

The MfM-U panel study was conducted in Erstfeld, a village of about 3800 habitants located in a Swiss Alpine valley, along which runs one of the major highways of Switzerland. From November 2007 to June 2009, thirteen children with doctor diagnosed asthma participated in monthly monitoring of pulmonary inflammation (*i.e.* fractional exhaled nitric oxide FeNO) and oxidative stress markers in breath condensate (*i.e.* nitrite, pH). During the whole study period, air pollution levels, including particulate matter ≤ 10µm (PM_{10}), nitrogen dioxide (NO_2), EC, OC, and particle numbers (PN), were monitored at one background, one highway and seven mobile sites distributed in the village. The spatiotemporal distribution of these pollutants was examined and NO_2 measurements were used to build a model estimating home outdoor concentrations at the participating children's homes. A similar approach as in the Southern California study was used by adding the background measurements to the model. Model estimates were then compared with 14-day integrated NO_2 concentrations measured outside the children's homes and at nine outdoor community sites. Chemically speciated data was used in receptor modeling to apportion the source contributions to PM_{10}. Both, NO_2 model estimates and source-specific PM_{10} was then used to investigate associations to pulmonary inflammation and oxidative stress marker levels in the children.

Results

In the Southern California study, city-specific and pooled models could explain a large part of variation for home outdoor $PM_{2.5}$, OC and EC with adjusted R^2 from 0.75 to 0.97. Important predictors were central site measurement, distance to highway and wind variables. City-specific OC and EC models performed better than pooled models. Daily personal $PM_{2.5}$ exposure correlated well with the predicted home outdoor concentrations (R^2 of 0.65 to 0.69) for city-specific and pooled models. However, daily personal OC or EC exposure was poorly approximated by home outdoor estimates.

In the MfM-U study, traffic-related pollutants NO_2, EC and PN showed distinct spatial patterns with high concentrations at the highway site decaying some 30-40% to background levels within 150-200m, while PM_{10} and OC were more homogeneously distributed. Weekday patterns of the traffic pollutants followed clearly the heavy-duty truck traffic counts on the highway. All pollutants showed higher concentrations in winter than in summer.

Adding background measurements to the NO_2 prediction model increased the variance explained (adjusted R^2) from 70% to 91%. Main predictors were background NO_2, inverse distance-weighted traffic counts and wind factors. Model estimates matched very well (R^2 = 0.74) the measured 14-day concentrations at the children's homes and additional community sites.

We could identify nine sources contributing to PM_{10}. Traffic (29%) was the main source, including traffic exhaust (18%), road dust (8%), tire & brake wear (1%), and road salt (2%). Other contributions came from secondary particles (27%), biomass burning (18%), railway traffic (11%) and mineral sources from mineral dust (7%) and a tunnel construction site (6%). Seasonal differences were observed with higher contributions from secondary particles (37%) in summer and from biomass burning (26%) and traffic (30%) in the winter. Traffic, railway and mineral contributions to PM_{10} also showed spatial differences with higher contributions at sites close to the specific source. Biomass burning estimates were highly correlated (R^2 = 0.81) with levoglucosan, a wood burning marker, while traffic exhaust estimates showed only a week association (R^2=0.13) with the diesel exhaust marker 1-nitropyrine due to the mixture of diesel and gasoline

in the traffic fleet. Also secondary pollutant contributions were only moderately correlated with nitro-polycyclic aromatic hydrocarbons.

Mean levels of fractional exhaled nitric oxide (FeNO), exhaled breath condensate (eBC) nitrite, and eBC pH measured in the thirteen children were 17.04ppb, 0.82µM, and 7.06, respectively, indicative for mild asthma. For days, when children did not report any cold symptoms, FeNO levels increased by 15%, 13% and 6% if NO_2, EC and total PM_{10} on the prior day of the health measurement were increased by one inter quartile range (IQR), respectively. Breath condensate pH levels decreased significantly with increasing PM_{10}, NO_2, and EC concentrations measured one, two or three days prior the health monitoring. However, no significant associations were observed between source-specific PM_{10} concentrations and FeNO, and between eBC nitrite and any of the pollutants.

Conclusions and outlook

We were able to build models to estimate residential outdoor air pollution exposure using only a limited number of spatially distributed monitoring sites. These modeling approaches could be applied to other studies, where extensive exposure measurements are not available.

We could identify traffic as the major source contributing to PM_{10} in Erstfeld and observed a distinct relationship between highway traffic and concentration levels of NO_2, EC and PN. In Switzerland, air pollution levels largely decreased during the last two decades. However, we still detected associations between traffic-related air pollution and pulmonary inflammation markers in children with asthma. This is of relevance for regulatory authorities defining air pollution standards to protect public health and the environment from adverse effects of air pollution. However, due to the lack of knowledge in pathways between air pollution and health outcomes, further epidemiological studies, especially relating source-specific air pollution exposure to health, as well as toxicological and epigenetic studies should be done.

Zusammenfassung

Hintergrund

Es ist belegt, dass Schadstoffe in der Luft einen Einfluss auf Lungen- und Herzkrankheiten haben. Durch die Urbanisierung der heutigen Gesellschaft nimmt verkehrsbedingte Luftverschmutzung eine besondere Stellung ein. Vor allem Kinder mit Asthma sind von den Folgen betroffen, mit häufiger auftretenden asthmatischen Symptomen und verminderten Lungenfunktionen. Neue Messmethoden zur Bestimmung verschiedener Entzündungsindikatoren in der Lunge erlauben eine Analyse der kurzfristigen Effekte von Luftschadstoffen auf die Gesundheit.

Die Bevölkerung ist normalerweise nicht nur einem einzelnen Luftschadstoff ausgesetzt, sondern einem Schadstoffgemisch aus verschiedenen Quellen. Die Schadstoffbelastung der einzelnen Personen wird in klassischen epidemiologischen Studien meist mit Luftschadstoffmessungen an einer zentralen Messstelle approximiert. Diese können aber die räumliche Verteilung der Schadstoffe nicht wiedergeben. Deshalb werden nun öfters Modelle entwickelt, die auch die räumliche Komponente enthalten.

Ziele

Die Ziele dieser Dissertation sind (1) Modelle zu berechnen, die verkehrsbedingte Luftschadstoffkonzentrationen in den bewohnten Gebieten abschätzen können, (2) die zu Feinstaub (PM_{10}) beitragenden Quellen und deren Anteile zu berechnen, und (3) den Einfluss dieser Luftschadstoffe auf die Gesundheit von Kindern mit Asthma zu prüfen.

Methoden

Diese Dissertation wurde im Rahmen von zwei Längsschnittstudien mit asthmatischen Kindern durchgeführt: einer Studie in der Region von Los Angeles und der MfM-U (Monitoring flankierende Massnahmen – Umwelt) Studie in einem Schweizer Alpental.

In der Kalifornischen Studie haben 63 Kinder aus Riverside und Whittier persönliche Luftschadstoffmessungen durchgeführt. Riverside erhält vor allem vom Wind transportierte Luftschadstoffe aus der Los Angeles Region, während Whittier eher vom lokalen Verkehr beeinflusst wird. Vom August bis Dezember 2003 (Riverside) und vom Juli bis November 2004 (Whittier) wurde in jeder Gemeinde acht Messintervalle von je 10 Tagen durchgeführt, während denen bei den Kindern die persönliche Exposition zu Feinstaub mit einem Durchmesser ≤2.5µm ($PM_{2.5}$), elementarem (EC) und organischem Kohlenstoff (OC) gemessen wurden. Gleichzeitig wurden die Luftschadstoffkonzentrationen auch bei je einem Kind zu Hause und an einer zentralen Messstelle gemessen. Der Anteil der vom lokalen Verkehr verursachten Luftbelastung bei den Kindern zu Hause wurde mit Hilfe des CALINE4 Dispersionsmodell berechnet. Die Luftschadstoffmessungen bei den Kindern zu Hause wurden dann benutzt, um bei den anderen Kindern, bei denen keine Messungen zu Hause gemacht wurden, die Konzentrationen von $PM_{2.5}$, EC, and OC zu berechnen. Wir benutzen Landnutzungs-Regressions Modelle, die wir mit Hintergrundmessungen und Schätzungen von dem CALINE4 Dispersionsmodell verfeinerten. Dabei untersuchten wir lokale wie auch regionale Modelle. Die Modellschätzungen wurden dann mit den persönlichen Luftschadstoffkonzentrationen verglichen.

Die MfM-U Studie wurde in Erstfeld durchgeführt, einer kleinen Gemeinde in einem Schweizer Alpental, durch das die Gotthardautobahn führt. Bei dreizehn Kindern mit Asthma wurden von November 2007 bis Juni 2008 monatliche Messungen von ausgeatmetem Stickoxid (FeNO) sowie dem pH Wert und des Nitrit Gehalts im Atemkondensat (eBC) gemacht, die alle den Entzündungsstatus in der Lunge beschreiben. Während der ganzen Studiendauer wurden an einer Hintergrundstation, einer Station nahe der Autobahn und sieben in der Gemeinde verteilten Messstationen Konzentrationen von Feinstaub mit einem Durchmesser ≤10µm (PM_{10}), Stickstoffdioxid (NO_2), EC, OC und Anzahl ultrafeiner Partikel (PN) gemessen. Wir untersuchten die räumlich-zeitliche Verteilung der verschiedenen Schadstoffe. Die gemessenen NO_2 Konzentrationen wurden dann in einem verfeinerten Landnutzungs-Regressions Modell benutzt, um die Schadstoffkonzentrationen bei den Studienteilnehmern zu Hause zu berechnen. Die Modellschätzungen wurden dann mit Passivsammler-Messungen bei den

Studienteilnehmern zu Hause verglichen. Der auf seine chemischen Element analysierte Feinstaub wurde benutzt, um die Quellen und deren Beitrag zum Feinstaub zu bestimmen. Diese Resultate sowie die NO_2 Schätzungen wurden dann benutzt, um den Einfluss dieser Schadstoffe auf die Gesundheit der Kinder zu analysieren.

Resultate

Die lokalen und regionalen Modelle in der Kalifonischen Studie konnten eine grossen Teil der Variationen von $PM_{2.5}$, OC und EC bei den Kindern zu Hause erklären (ajustierte R^2 von 0.75 – 0.97). Die wichtigsten Parameter in den Modellen waren die Hintergrund Konzentrationen, die Distanz zu einer Autobahn und verschiedene Windfaktoren. Für OC und EC lieferten die lokalen Modelle bessere Resultate als die regionalen Modelle. Die $PM_{2.5}$ Konzentrationen von den persönlichen Messungen korrelierten sehr gut mit den modellierten Schätzungen (R^2 von 0.65 – 0.69) für beide, lokale wie regionale Modelle. Für OC und EC Messungen waren die Korrelationen schlecht.

In der MfM-U Studie konnte gezeigt werden, dass die verkehrsabhängigen Luftschadstoffe NO_2, EC und PN stark von der Distanz zur Autobahn abhängig sind. Sie nehmen innerhalb von 150-200 Meter Distanz zur Autobahn um ca. 30-40% ab und verharren dann auf einem Hintergrundniveau. PM_{10} und OC hingegen zeigten eine uniforme räumliche Verteilung. Die Wochengänge von NO_2, EC und PN zeigten denselben Verlauf wie die Anzahl der Schwerverkehrs-fahrzeuge auf der Autobahn. Alle Schadstoffkonzentrationen waren höher im Winter als im Sommer.

Das Verfeinern des Landnutzungs-Regressionsmodells mit gemessenen Hintergrundkonzentrationen verbesserte die erklärte Varianz von 70% auf 91%. Haupteinflussfaktoren waren die Hintergrundkonzentrationen, mit der Distanz gewichtete Verkehrszahlen und Windfaktoren. Der Vergleich von den Modellschätzungen mit den gemessenen 14-Tage Konzentrationen bei den Kindern zu Hause war mit einem R^2 von 0.74 sehr gut.

In Erstfeld konnten wir neun Quellen von Feinstaub identifizieren. Den wichtigsten Beitrag lieferte der Verkehr (29%), bestehend aus Verkehrsabgasen

(18%), Strassenstaub (8%), Pneu- und Bremsabrieb (1%) und Streusalz (2%). Auch Partikel von sekundären Schadstoffen (27%), Holzfeuerungen (18%), Eisenbahnverkehr (11%) und Mineralien von herumgewirbeltem Staub (7%) und den Tunnelbaustelle (6%) trugen zur Feinstaubbelastung bei. Beiträge von sekundären Partikeln waren mit 37% höher im Sommer, während Holzfeuerungen (26%) und der Verkehr (30%) im Winter mehr beitrugen. Räumliche Unterschiede fanden wir für Verkehr, Eisenbahn und Mineralien, die jeweils höhere Beiträge an den Messstationen zeigten, die am nächsten bei der Quelle waren. Wir fanden gute Korrelationen zwischen Beiträgen von Holzfeuerungen und dem Indikator Levoglucosan (R^2=0.81), während Beiträge von Verkehrsabgasen weniger gut mit dem Dieselindikator 1-Nitropyrin korrelierten (R^2=0.13), was an der Durchmischung der Verkehrsflotte mit Diesel und Benzin Fahrzeugen liegt.

Die dreizehn Kinder zeigten im Durchschnitt Werte von 17.04ppb, 0.82µM, and 7.06 für FeNO, eBC Nitrit und eBC pH. An Tagen, an denen die Kinder keine Erkältungssymptome zeigten, stieg ihr FeNO Wert um 15%, 13% und 6%, wenn die Vortageskonzentration von NO_2, EC und PN um einen Quartilsabstand erhöht waren. Gleichzeitig sank auch der eBC pH Wert signifikant. Zwischen quellenspezifischem Feinstaub und FeNO konnten wir keinen Zusammenhang finden, auch nicht für eBC Nitrit und irgend einem Luftschadstoff.

Schlussfolgerungen und Ausblick

In dieser Arbeit konnten wir Modelle generieren, die uns erlaubten mit Daten von wenigen räumlich verteilten Messstationen die Luftschadstoffkonzentrationen auch an den verschiedenen Wohnorten der Studienteilnehmer zu berechnen. Die verwendeten Methoden können leicht auf andere Studien übertragen werden, in denen detaillierte Expositionsmessungen nicht möglich sind.

Wir identifizierten den Verkehr als Hauptquelle für die Feinstaubbelastung in Erstfeld und fanden einen deutlichen Zusammenhang zwischen den Schwerverkehrszahlen auf der Autobahn und den Luftschadstoffen NO_2, EC und PN. Durchschnittliche Luftschadstoffwerte sanken in den letzten zwanzig Jahren kontinuierlich in der Schweiz. Trotzdem konnten wir bei asthmatischen Kindern

Zusammenhänge zwischen Entzündungsindikatoren in der Lunge und verkehrsbedingten Luftschadstoffbelastungen finden. Diese Resultate sind von besonderer Bedeutung für Ämter, die für die Regulierung der Schadstoffe verantwortlich sind, um die Umwelt die die Gesundheit der Bevölkerung zu schützen. Da die Prozesse, die von den Schadstoffen zu den gesundheitlichen Auswirkungen führen, immer noch nicht klar sind, sollten in Zukunft weitere epidemiologische Studien unternommen werden, die vor allem auch den Fokus auf quellenspezifische Schadstoffe legen sollten. Zusätzlich sollten auch die toxikologischen und epigenetischen Studien weitergeführt werden.

List of abbreviations

eBC	Exhaled breath condensate
EC	Elemental carbon
FeNO	Fractional exhaled nitric oxide
FEV_1	Forced expiratory volume in 1 second (lung function)
FVC	Forced vital capacity (lung function)
H_2O_2	Hydrogen peroxide
IQR	Interquartile range
lag 1 / lag 1,2	The day before the health measurement / the average of the two days prior the health measurement
LUR	Land-use regression
MfM-U	Monitoring of Supporting Measures - Environment (Monitoring flankierende Massnahmen – Umwelt), a project funded by the Swiss Federal Office of the Environment
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides, including NO and NO2
O_3	Ozone
OC	Organic carbon
PM_{10}	Particulate matter with aerodynamic diameter <10µm
$PM_{2.5}$	Particulate matter with aerodynamic diameter <2.5µm
PMF	Positive Matrix Factorisation
PN	Particle number concentration
SO_2	Sulfur dioxide
VOC	Volatile organic compound

1. Introduction and background

Clean air is nowadays considered to be a basic requirement of human health and well-being (WHO, 2006). This recently developed awareness has grown on multiple scientific evidence that air pollution represents a significant and unequivocal adverse health factor and increases the risk of respiratory and cardiovascular diseases. It is noteworthy that the link between air pollution and enhanced death rate was already evident as early as in the 17th century in densely populated cities such as London, peaking with the "Great Smog of 1952" claiming more than 4000 deaths in the weeks following it (US EPA, 2012). Such events forced governments and public authorities to pass laws and regulations to protect public health, especially for susceptible groups such as elderly people, asthmatics and children, leading in the 1970's to the instating of environmental and public agencies to monitor and set limits of pollutant levels in the atmosphere. Supranational organizations such as the World Health Organization (WHO) have reviewed epidemiological studies that serve as guidance to evaluate and set air quality guidelines worldwide. In the last 40 years, concerted efforts, mostly in developed countries, have significantly curbed the emission of particulate matter (in fact, establishing the central heating system in densely lived areas), reduced the levels of SO_2 in burning fuels (indirectly saving central European forests decimated by acid rains) and controlled the release of other pollutants such as nitrogen oxides, carbon monoxide and heavy metals in our environment.

Despite these early successes, which can be estimated by the number of people living longer and healthier lives than they would have in the absence of regulations (US: in 2020, 230'000 people/year, (Kinney and Nori-Sarma, 2011)), much remains to be done, especially with the ever raising worldwide population and its increased industrialization rate. The WHO estimates that more than 2 million premature deaths each year can be attributed to the effects of air pollution with more than half of this disease burden borne by the populations of developing countries (WHO, 2006). In the last 10 years, new data on air pollution have

demonstrated that populations are usually not exposed to one but rather to a mixture of pollutants emitted by various sources with different spatiotemporal concentration ranges that might have not been appropriately captured in classical epidemiological studies typically conducted with one central measurement. In particular, the systematic use of modeling promises a much more spatial- and time-resolved picture of the pollutant (or a set of pollutants) which are hypothesized to cause an adverse health effect on a group of individuals.

The following paragraphs summarize air pollution related health effects, characteristics and sources of some selected air pollutants, and exposure modeling approaches used in epidemiological studies.

1.1. Air pollution and health

Air pollution has been extensively documented to increase the risk of respiratory and cardiovascular diseases (Brunekreef and Holgate, 2002; Kuenzli and Tager, 2005; Pope and Dockery, 2006; Sarnat and Holguin, 2007; Kuenzli et al., 2010). Commonly observed symptoms may include difficulty in breathing, wheezing, coughing and aggravation of existing respiratory and cardiac conditions, typically resulting in increased medication use and consumption of medical services. Importantly, individual reaction to air pollutants is dependent on the type of pollutant a person is exposed to, the degree of exposure, the individual's health status and genetics. Traffic-related air pollution, in particular, has been extensively studied (Health Effects Institute, 2010). It has been associated in children with higher prevalence of asthma and related symptoms (Brauer et al., 2007; Morgenstern et al., 2007; Jerrett et al., 2008), and reduced lung function (Brunekreef et al., 1997; Gauderman et al., 2007), which also result in economic consequences (Brandt et al., 2012).

The reporting of health outcomes in asthmatics is typically carried out through questionnaires wherein the subject is asked to rate his symptoms and the use of medication. In addition, objective health measurements may include lung function tests, such as forced vital capacity (FVC) or forced expiratory volume in 1 second (FEV_1) (Derom et al., 2008). Fractional exhaled nitric oxide (FeNO) also provides a well-established, non-invasive method to diagnose and monitor asthma in children (Pijnenburg and De Jongste, 2008). In recent years, there has been an increasing interest to study inflammatory biomarkers in exhaled breath, which can be easily collected in children. However, there is still no established standard for the collection of such samples (Horvath et al., 2005; Hunt, 2007; Kullmann et al., 2007).

Most epidemiological studies monitoring health effects in asthmatic children have reported distance to roads, traffic density, or measured/modeled NO_2 and soot levels as exposure metric for traffic-related air pollution (see 1.3).Only few of them have dealt with acute health effects related to source- or chemical species-specific exposure (Solomon et al.; Sarnat et al., 2008).

1.2. Air pollution characteristics and sources

Air pollutants have been categorized through their physicochemical characteristics and by their source of origin. While they can be either emitted directly into the atmosphere (primary pollutants) or formed by primary pollutants reacting or interacting within the atmosphere itself (secondary pollutants), they are present either in the form of gases or vapors or as material in solid or liquid phase suspended in the atmosphere (particulate pollutants). Air pollutants are produced both from natural (*e.g.* dust, volcanoes, sea spray) or anthropogenic (*e.g.* traffic, biomass burning, industrial plants, construction sites) sources. Sources and physical characteristics of some of the major pollutants are described in Table 1-1.

In contrast to single gases, particulate matter (PM) comprises a complex group of particles and droplets with varying sizes and composition (Seinfeld and Pandis, 2006). PM is usually categorized by size ranges based on the aerodynamic diameter of the particles (Figure 1-1). PM_{10} includes all particles with a diameter ≤ 10µm and is subdivided into "coarse particles" $PM_{2.5–10}$ (particles with diameter of 2.5-10µm, mainly erosion minerals) and "fine particles" $PM_{2.5}$ (particles with diameter ≤ 2.5µm, mainly particles directly emitted from combustion processes). Ultrafine particles comprise particles with a diameter ≤1µm (PM_1), normally in the 1-100 nm range. They are usually measured and reported in particle number concentration as their mass concentrations are typically very low. Ultrafine particles mainly have their origin in primary emissions from combustion-related sources. They have a very short lifetime (minutes to hours) and they grow rapidly into the $PM_{2.5}$ range by coagulation and condensation (Seinfeld and Pandis, 2006). Therefore they show large gradients in their spatial distribution (Zhu et al., 2002).

Table 1-1: Sources and physical characteristics of some major air pollutants (Seinfeld and Pandis, 2006; Kuenzli et al., 2010).

Pollutants	**Physical characteristics**	**Sources and formation**
Primary pollutants		
Sulfur dioxide (SO_2)	Gas	Formation: combustion of sulfur containing fuels; extraction of metals from ore. Sources: oil, coal, and in some countries diesel. SO_2 is a precursor for secondary air pollution.
Nitrogen oxides (NO_x), incl. nitric oxide (NO) and nitrogen dioxide (NO_2)	Highly reactive gases	Formation: high-temperature combustion. Sources: mainly traffic NO_x are important precursors for secondary air pollution.
Volatile organic compounds (VOC), incl. wide range of hydrocarbons, oxygenates, halogenates and other carbon compounds	Gas	Formation: direct vaporization into the atmosphere, as their vapor pressure at room temperature is sufficiently high. Sources: fuel vapors, natural gas, methane and solvents. VOCs are precursors for ozone (O_3)
Particulate matter (PM), incl. elemental and organic carbon (EC and OC)	Particles and droplets suspended in air	Formation: fossil fuel and biomass combustion and erosion processes. Sources: traffic, industrial boilers, wild fires, domestic heating, cooking, soil, dust, construction or demolition activities, farming, resuspended road dust, windstorms, volcanoes, sea salt, pollen, molds, and other biological material.
Secondary pollutants		
Particulate matter (PM), incl. sulfate, nitrate and secondary organic aerosols (SOA)	Particles and droplets suspended in air	Formation: by reactions from precursor gases (*i.e.* SO_2, NO_x, ammonia and VOCs) in the atmosphere. Sources: the same sources as for precursor gases, mainly traffic
Ground level ozone (O_3)	Gas	Formation: by photochemical reactions from precursor gases NO_x and VOCs in the atmosphere.

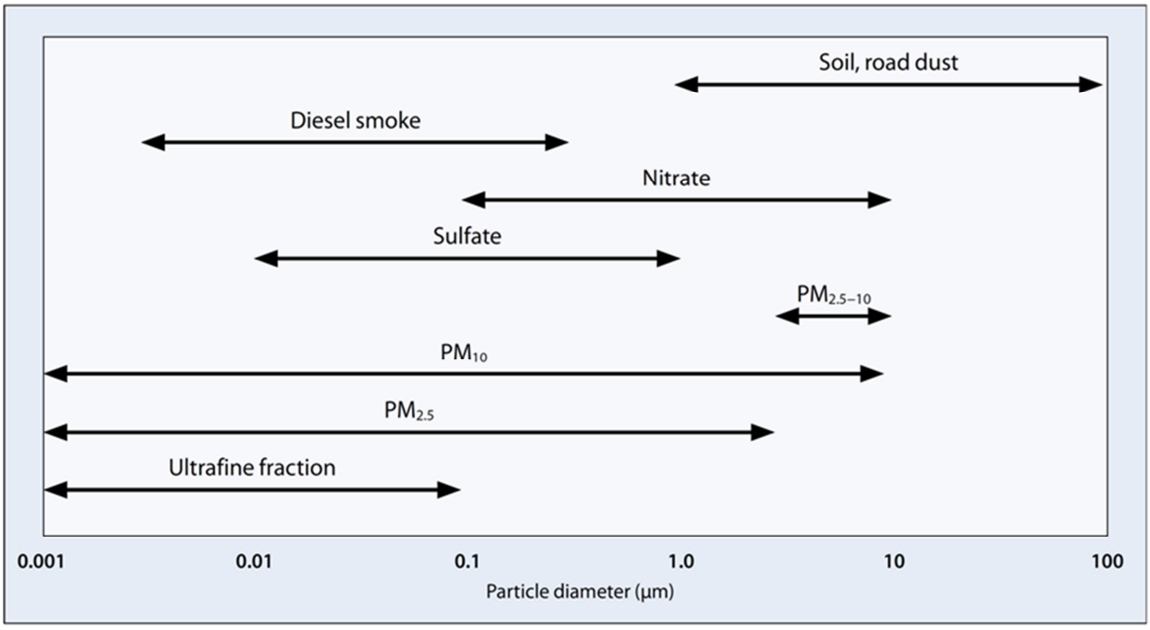


Figure 1-1: Size range of airborne particles, showing the health-related ultrafine, $PM_{2.5}$ and PM_{10} fractions and the typical size range of some major components. (WHO, 2006)

Air quality guidelines and standards aim at protecting public health and the environment from the adverse effects of air pollution. National regulatory authorities regularly review and set standards to define the acceptable air pollution levels. Therefore standards may vary with location. Table 1-2 displays some current standards.

Table 1-2: Air quality standards set by different authorities.

Source	SO_2 (µg/m³)				NO_2 (µg/m³)			PM_{10} (µg/m³)		$PM_{2.5}$ (µg/m³)		O_3 (µg/m³)	
	1 year	24 hours	1 hour	10 min	1 year	24 hours	1 hour	1 year	24 hours	1 year	24 hours	8 hours	1 hour
WHO[1]		20		500	40		200	20	50[a]	10	25[a]	100	
European Union[2]		125[a]	350[b]		40		200[c]	40	50[d]	25		120	
Switzerland[3]	30	100[e]			30	80[e]		20	50[e]				120[e]
United States[4]			200		100		190		150[e]	15	35	150	
California[5]		105	665		57		344	20	50	12		140	180

[(a)]: not to be exceeded more than 3 days per year; [(b)]: not to be exceeded more than 24 times per year; [(c)]: not to be exceeded more than 18 times per year; [(d)]: not to be exceeded more than 35 days per year; [(e)]: not to be exceeded more than once per year;

[(1)]: (WHO, 2006); [(2)]: (European Parliament, 2008); [(3)]: (Swiss Confederation, 1998); [(4)]: (US EPA);

[(5)]: (California Air Resources Board);

1.3. Air pollution modeling

Spatial models

Spatial distribution of air pollution can vary drastically depending on the type of source considered and the pollutant(s) of interest. Sources can be categorized as point source (*e.g.* industrial sites), line source (*e.g.* traffic), or area-source (*e.g.* domestic heating). Pollution levels emitted from point and line sources usually show spatial gradients while area source-related concentrations are more homogeneously distributed. These different behaviors can lead to large discrepancies between pollution levels measured at central monitoring stations (typical for routine monitoring) and what would be actually measured for example at a residential site (Goswami et al., 2002; Zhu et al., 2002). Modern epidemiologic studies are now taking advantage of modeling to predict more accurately gradients of pollutant concentrations in the study area of interest (Brauer et al., 2003; Jerrett et al., 2004; Hoek et al., 2008). Some of those most popular models are described below:

Proximity models

Proximity models assumes that population exposure is at its highest when it is closest to the emission source. This strategy is usually applied to generate buffer areas around roads to classify subjects as exposed or not exposed, depending on their being within or outside the buffer area.

Interpolation

Interpolation models require several monitoring stations to measure the distribution of a target pollutant throughout the study region. These measurements can then be used with geostatistical techniques, such as kriging (Jerrett et al., 2001), to enable the estimation of the pollutant concentrations in the centers of a grid, which is imposed over the study area.

Land-use regression (LUR) models

LUR models use least-squares regression to predict pollution concentrations using air pollution data from fixed monitoring stations as dependent variable and surrounding land use parameters and traffic characteristics as independent

variables. Air pollution concentrations can then also be estimated at other locations of the study as long as land use and traffic characteristics are also known.

Dispersion models

Gaussian plume dispersion models are often used in epidemiological studies. They assume a Gaussian distribution of the pollution levels from a point or a line source. Data from emission inventories, meteorology and topography are used to estimate spatially-refined concentration estimates of the pollutants.

Combined models

Combined models use either temporally refined personal or regional monitoring data to introduce a temporal component to one of the above described empirical models (Brauer, 2010) so that short-term (*e.g.* daily, weekly, bi-weekly, etc.) air pollution models can be generated.

All above described model approaches enable the prediction of pollutant concentrations at the home outdoor level. However, calculation of personal exposure to air pollution requires additional complexity as people move through various microenvironments. Also, many indoor environments comprise additional pollution sources (*e.g.* cooking, candle burning, passive smoke, paint fumes) that can influence exposure (Dales et al., 2008)

Source apportionment

Exposure to PM has been reported to be associated with different cardiopulmonary health outcomes (Davidson et al., 2005; Anderson et al., 2012). However, it remains unclear which characteristics or components of PM might be responsible for the differentiated health outcomes, which might have been caused by single chemical components, by several groups of particles emitted by single sources, or by a combination of both. A number of studies on source-specific PM effects on health have been conducted in the last decade to clarify this point (De Kok et al., 2006; Schlesinger et al., 2006; Chen and Lippmann, 2009; Stanek et al., 2011).

In parallel, statistical models were developed to apportion the contributions of different sources to PM concentrations, the so-called receptor models (Paatero and Tapper, 1994; Hopke, 2003; Reff et al., 2007; Viana et al., 2008). The fundamental principle behind receptor modeling is the conservation of mass, *i.e.* the measured PM mass is equal to the sum of contributions of all sources:

$$c_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + \varepsilon_{ij} \qquad (1)$$

where c_{ij} is the concentration of the chemical species j in sample i, g_{ik} is the concentration of PM mass contributed by source k in sample I (source contribution), and f_{kj} is the mass fraction of species j in PM from source k (source profile).

There are various models available depending on whether the source profiles are known or not. Chemical Mass Balance and other multivariable calibration models (*e.g.* Partial Least Squares, Genetic Algorithms) require knowledge about the source profiles while Principal Component Analysis, UNMIX, Multilinear Engine, and Positive Matrix Factorization (PMF) do not.

PMF, which was used in this thesis, is a receptor model, which solves a positively constrained bilinear mass balance model (*i.e.* the chemical species cannot give negative contributions to the source profiles and the sources cannot give negative mass contributions, Equation 1) based on a weighted least squares fit (Paatero and Tapper, 1994; Paatero, 1997).

1.4. Aims

The overall aim of this thesis is to build models for estimating residential outdoor exposure to traffic-related air pollution and to use them for assessment of associated health effects in children with asthma. In particular, the research aims of this thesis were delineated around the framework of two pediatric asthma panel studies: the Southern California study, supported by the National Institute of Environmental Health Sciences (ES11615) of the U.S. National Institutes of Health (NIH); and the MfM-U (Monitoring flankierende Massnahmen – Umwelt) study, funded by the Federal Office for the Environment FOEN (No. 050303 /516 G161-1955) of the Swiss Government.

The following research questions were addressed:

Question 1: Can we predict residential outdoor exposure to different traffic-related air pollutants and are the estimates representative for personal exposure?

Specific aims:

I. To assess the spatial and temporal distribution of different air pollutants.

II. To model short-term outdoor exposure to traffic-related air pollutants in different topographic settings.

III. To compare the model estimates with personal and home outdoor measurements.

Findings are presented in Chapter 2, containing Article 1 (“Examining the representativeness of home outdoor $PM_{2.5}$, EC, and OC estimates for daily personal exposures in Southern California”) and Article 2 (“Role of highway traffic on spatial and temporal distributions of air pollutants in a Swiss Alpine valley”). In both articles, short-term models for traffic-related air pollution were built, taking into consideration the respective topographic conditions of the three study sites,

Riverside and Whittier in Southern California, as well as Erstfeld in a Swiss Alpine valley. The model performance was validated by personal (Article 1) and home outdoor measurements (Article 2).

Question 2: What are the different sources of PM10 in a highway impacted Alpine valley and how much do they contribute to ambient PM10?

Specific aims:

I. To find and apportion sources of PM10 using receptor modeling.

II. To assess the spatial and temporal distribution of source-specific PM10.

Findings are presented in Article 3 ("Source Contribution to PM10 in a Highway Impacted Swiss Alpine Valley") (Chapter 3).

Question 3: Are there any acute pulmonary health effects in children with asthma due to highway traffic-specific exposure?

Specific aims:

I. To find associations between levels of daily residential outdoor air pollution and changes in pulmonary inflammation markers.

II. To find associations between levels of source-specific PM10 and changes in pulmonary inflammation markers.

Results are presented in Chapter 4, dealing with the different biomarker measurements and their changes associated with short-term modeled (Article 2) and source-specific (Article 3) air pollution exposure.

1.5. Framework and methods

The research aims of this thesis were developed in the framework of two pediatric asthma panel studies. The scopes of the studies and the methods used to analyze them are briefly presented below.

Southern California study

This panel study was initiated to assess acute effects on pediatric asthma by particulate air pollution and NO_2 in the vicinity of a large North-American city. Continuous measurements of personal air pollution exposure were collected in 63 children living in Riverside and Whittier, two cities with high air pollution levels in the Los Angeles basin. Riverside is a smog receptor site downwind from urban Los Angeles, while Whittier is a site immediately downwind of vehicular emission sources. From August to December 2003 (Riverside) and from July to November 2004 (Whittier), eight 10-day monitoring periods of personal measurements of $PM_{2.5}$, EC, and OC were conducted in each city. In parallel, one home site and a fixed central site were monitored concurrently during the same monitoring period. Also, local traffic-related air pollution contributions at each home were estimated with the CALINE4 dispersion model. Delfino and co-workers (Delfino et al., 2006, 2008) reported increased fractional exhaled nitric oxide (FeNO) and decreased lung function in those asthmatic children correlating with increased personal air pollution exposure, whereas ambient air pollution showed lesser or no effects.

In this study, measured home outdoor concentrations, which were only collected for part of the participating children, were used to build models estimating $PM_{2.5}$, EC, and OC concentrations at all other participating children's homes. Models were built by land-use regression (LUR) methods and included typical LUR model variables (*e.g.* population density, distance to roads) as well as temporal variables such as daily measurements at the central site, inverse distance weighted traffic counts, wind variables, and the CALINE4 estimates. City-specific and combined models were analyzed. Model predictions were then compared with the personal measurements.

MfM-U (Monitoring flankierende Massnahmen – Umwelt) project

The MfM-U project aims at monitoring the effectiveness of the actions taken to minimize the impact of trans-alpine highway traffic on the environment and public health since the implementation of the Traffic Relocation Act in Switzerland in 2001. Earlier health studies within this project have reported increased bronchitis and asthmatic symptoms in adults and children related to highway-traffic exposure (Ragettli, 2009; Hazenkamp-von Arx et al., 2011). For this thesis, a pediatric asthma panel study was conducted in a community in the Swiss Alps which is affected by a highway with the aims of (1) modeling traffic-related residential outdoor exposure, (2) finding and apportioning sources of PM_{10}, and (3) investigating associations between health measurements and the under (1) and (2) estimated air pollution exposures.

This study was carried out in Erstfeld, a community of about 3800 habitants located in an 800 to 900 meter wide Swiss Alpine valley, along which runs one of the major highways of Switzerland. Thirteen children with doctor diagnosed asthma were monthly monitored from November 2007 to June 2009 for inflammation and oxidative stress markers (*i.e.* fractional exhaled nitric oxide (FeNO), biomarkers in exhaled breath condensate). At the same time, an extensive air pollution monitoring, including PM_{10}, NO_2, EC, OC, and particle numbers (PN), was carried out at one background, one highway and seven mobile sites distributed in the village. In addition, 14-day integrated NO_2 levels were measured inside and outside the children's homes and at nine outdoor community sites.

The spatiotemporal distribution of each air pollutant was explored and compared to highway-traffic counts. NO_2 measurements at the highway and at the seven mobile sites were used to build a model estimating home outdoor concentrations at the participating children's homes. A similar approach as in the Southern California study was used but considering additionally specific meteorological conditions such as inversion episodes. The estimates were then compared with the 14-day outdoor measurements at the participants' homes. Source contributions to PM_{10} were determined by receptor modeling using the PMF method. Model estimates of NO_2 and source-specific PM_{10} were then used to assess short-term impacts on pulmonary inflammation and oxidative stress markers in the children.

2. Modeling of outdoor exposure to traffic-related air pollution

Article 1: Examining the representativeness of home outdoor PM2.5, EC, and OC estimates for daily personal exposures in Southern California

Regina E. Ducret-Stich[1,2], Ralph J. Delfino[3], Thomas Tjoa[3], Armin Gemperli[2], Alex Ineichen[1,2], Jun Wu[3], Harish C. Phuleria[1,2], L.-J. Sally Liu[1,2,4]

[1] Department of Epidemiology and Public Health, Environmental Exposure Sciences, Swiss Tropical and Public Health Institute, Basel, Switzerland

[2] University of Basel, Basel, Switzerland

[3] Department of Epidemiology, School of Medicine, University of California, Irvine, CA, USA

[4] Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, WA, USA

This article has been published in the journal *Air Quality, Atmosphere & Health*

Air Qual Atmos Health (2012) 5:335–351
DOI 10.1007/s11869-010-0099-y

Examining the representativeness of home outdoor $PM_{2.5}$, EC, and OC estimates for daily personal exposures in Southern California

Regina E. Ducret-Stich · Ralph J. Delfino · Thomas Tjoa · Armin Gemperli · Alex Ineichen · Jun Wu · Harish C. Phuleria · L.-J. Sally Liu

Received: 6 March 2010 / Accepted: 2 September 2010 / Published online: 15 October 2010

Abstract Recent studies have linked acute respiratory and cardiovascular outcomes to measurements or estimates of traffic-related air pollutants at homes or schools. However, few studies have evaluated these outdoor measurements and estimates against personal exposure measurements. We compared measured and modeled home outdoor concentrations with personal measurements of traffic-related air pollutants in the Los Angeles air basin (Whittier and Riverside). Personal exposure of 63 children with asthma and 15 homes were assessed for particulate matter with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$), elemental carbon (EC), and organic carbon (OC) during sixteen 10-day monitoring runs. Regression models to predict daily home outdoor $PM_{2.5}$, EC, and OC were constructed using home outdoor measurements, geographical and meteorological parameters, as well as CALINE4 estimates at outdoor home sites, which represent the concentrations from local traffic sources. These home outdoor models showed the variance explained (R^2) was 0.97 and 0.94 for $PM_{2.5}$, 0.91 and 0.83 for OC, and 0.76 and 0.87 for EC in Riverside and Whittier, respectively. The $PM_{2.5}$ outdoor estimates correlated well with the personal measurements (Riverside R^2=0.65 and Whittier R^2=0.69). However, excluding potentially inaccurate samples from Riverside, the correlation between personal exposure to carbonaceous species and home outdoor estimates in Whittier was moderate for EC (R^2=0.37) and poor for OC (R^2=0.08). The CALINE4 estimates alone were not correlated with personal measurements of EC or other pollutants. While home outdoor estimates provide good approximations for daily personal $PM_{2.5}$ exposure, they may not be adequate for estimating daily personal exposure to EC and OC.

Keywords Air pollution · Elemental carbon · Organic carbon · Exposure modeling · Traffic exhaust

Electronic supplementary material The online version of this article (doi:10.1007/s11869-010-0099-y) contains supplementary material, which is available to authorized users.

R. E. Ducret-Stich (✉) · A. Ineichen · H. C. Phuleria · L.-J. S. Liu
Department of Epidemiology and Public Health, Environmental Exposure Sciences, Swiss Tropical and Public Health Institute, P.O. Box 4002, Basel, Switzerland
e-mail: regina.ducret@unibas.ch

R. E. Ducret-Stich · A. Gemperli · A. Ineichen · H. C. Phuleria · L.-J. S. Liu
University of Basel,
Basel, Switzerland

R. J. Delfino · T. Tjoa · J. Wu
Department of Epidemiology, School of Medicine,
University of California,
Irvine, CA, USA

L.-J. S. Liu
Department of Environmental and Occupational Health Sciences,
University of Washington,
Seattle, WA, USA

Introduction

Numerous epidemiological studies have found associations between outdoor air pollution and adverse respiratory outcomes (Brunekreef and Holgate 2002; Pope and Dockery 2006). In particular, traffic-related air pollution has been found to affect respiratory health (Jansen et al. 2005; McCreanor et al. 2007; Meng et al. 2007) especially in children (Delfino et al. 2009; Koenig et al. 2005; Ryan et al. 2005; Ryan and LeMasters 2007; Sarnat and Holguin 2007; Trasande and Thurston 2005). In the Los Angeles (LA) area,

many houses and schools are close to major roads and freeways, increasing children's exposure to air pollution from traffic (Künzli et al. 2003). The Southern California Children's Health Study showed positive associations between exposure to long-term traffic-related air pollution and asthma prevalence in a pediatric cohort (Gauderman et al. 2005; McConnell et al. 2006) and negative effects on lung growth independent of background air pollution levels (Gauderman et al. 2007). A limited number of studies also linked acute respiratory effects to personal $PM_{2.5}$ exposure in children and adults (Delfino et al. 2004, 2006, 2008; Ebelt et al. 2005; Koenig et al. 2005; Strand et al. 2006; Trenga et al. 2006).

Due to the significant intra-urban spatial variation of traffic air pollution (Goswami et al. 2002; Liu et al. 2007; Zhu et al. 2002), exposure proxies or land-use regression models have been used to estimate long-term personal exposure to traffic pollutants in urban areas (Hoek et al. 2008; Jerrett et al. 2005). Despite broad applications of these methods, only Van Roosbroeck et al. (2006, 2007, 2008) have evaluated certain exposure proxies against personal exposure to soot. The land-use regression models have yet to be validated against personal exposure measurements. Additionally, it remains unclear whether these models are useful for estimating short-term (daily) personal exposure to traffic pollutants.

The present study aimed to address this issue by evaluating the ability of daily home outdoor air pollutant estimates from land-use regression models to represent daily personal exposure to air pollutants, including $PM_{2.5}$, EC, and OC. To our knowledge, this is the first study using personal OC measurements to validate model estimates for personal exposure to OC. We constructed land-use regression models for traffic pollutants outside homes using geographical parameters and outdoor pollutant measurements. CALINE4 model estimates for traffic pollutants were also incorporated and tested. These model predictions were compared against personal measurements in two cities with different ambient pollution source characteristics.

Method

Study design

This work was part of a panel study evaluating acute health outcomes of 63 children with asthma living in the cities of Riverside and Whittier in the LA air basin (Delfino et al. 2006, 2008; Fig. 1). Riverside is a smog receptor site downwind from urban LA (Kim et al. 2002; Na et al. 2004). There, 31 subjects were followed periodically from August through mid-December 2003. Whittier is a site immediately downwind of vehicular emission sources. There, 32 subjects were followed periodically from July through November 2004. In each city, eight 10-day exposure monitoring periods (runs) were conducted, consisting of four subjects with concurrent personal monitoring of $PM_{2.5}$ mass, EC, and OC. In each run, one subject's residence and a central site were monitored and modeled for concurrent $PM_{2.5}$ mass, EC, and OC (Fig. 1).

Exposure measurements

Personal exposure

The following measurements were made in each subject over the 10-day run. We measured 1-min average $PM_{2.5}$ using the personal DataRAM (MIE pDR-1200; Thermo Electron Corp., Franklin, MA, USA). The pDR is an integrated nephelometer with a 2.5-μm sharp-cut cyclone (BGI model GK 2.05, KTL cyclone, GI Inc., Waltham, MA, USA) operated at 4 L/min. It was carried by each subject in a specially designed soundproof backpack with separate compartments for the subject's school books. $PM_{2.5}$ mass was also collected on a 37-mm (back-up) quartz filter (Whatman Inc, Florham Park, NJ, USA), which was placed downstream of the pDR and collected particles over each of ten 24-h sampling periods. These filters were pre-baked prior to sampling to remove any carbon. Analysis for EC and OC was done using the thermal manganese dioxide oxidation protocol (Fung et al. 2002). A HOBO logger (Onset Computer Corp., Pocasset, MA, USA) was used to record 1-min relative humidity (RH) and temperature. All pDR data were adjusted for the effect of RH (Wu et al. 2005a). Continuous (1-min) and gravimetric (24-h) measurements of the personal sampler were validated by comparing them against each other and against reference methods (Chakrabarti et al. 2004). Continuous $PM_{2.5}$ measurements from the pDR were compared with collocated measurements from a Beta Attenuation Monitor (R^2=0.75, corrected for RH). Gravimetric measurements from the back-up filter of the pDR were compared with gravimetric measurements from a Partisol sampler (R^2=0.93) and with the 24-h average from the Beta Attenuation Monitor (R^2=0.71). The R^2 between the filter-based personal $PM_{2.5}$ and the continuous personal $PM_{2.5}$ (corrected for RH) was 0.56.

Fixed-site measurements

Concurrent with the personal measurements, simultaneous indoor and outdoor monitoring was conducted at one home and at a central site station during each of the sixteen 10-day runs. The central site in Riverside was the South Coast Air Quality Management District (SCAQMD) monitoring site, while in Whittier it was set up by us at one of the subjects' residences (Fig. 1). At all of these indoor, outdoor,

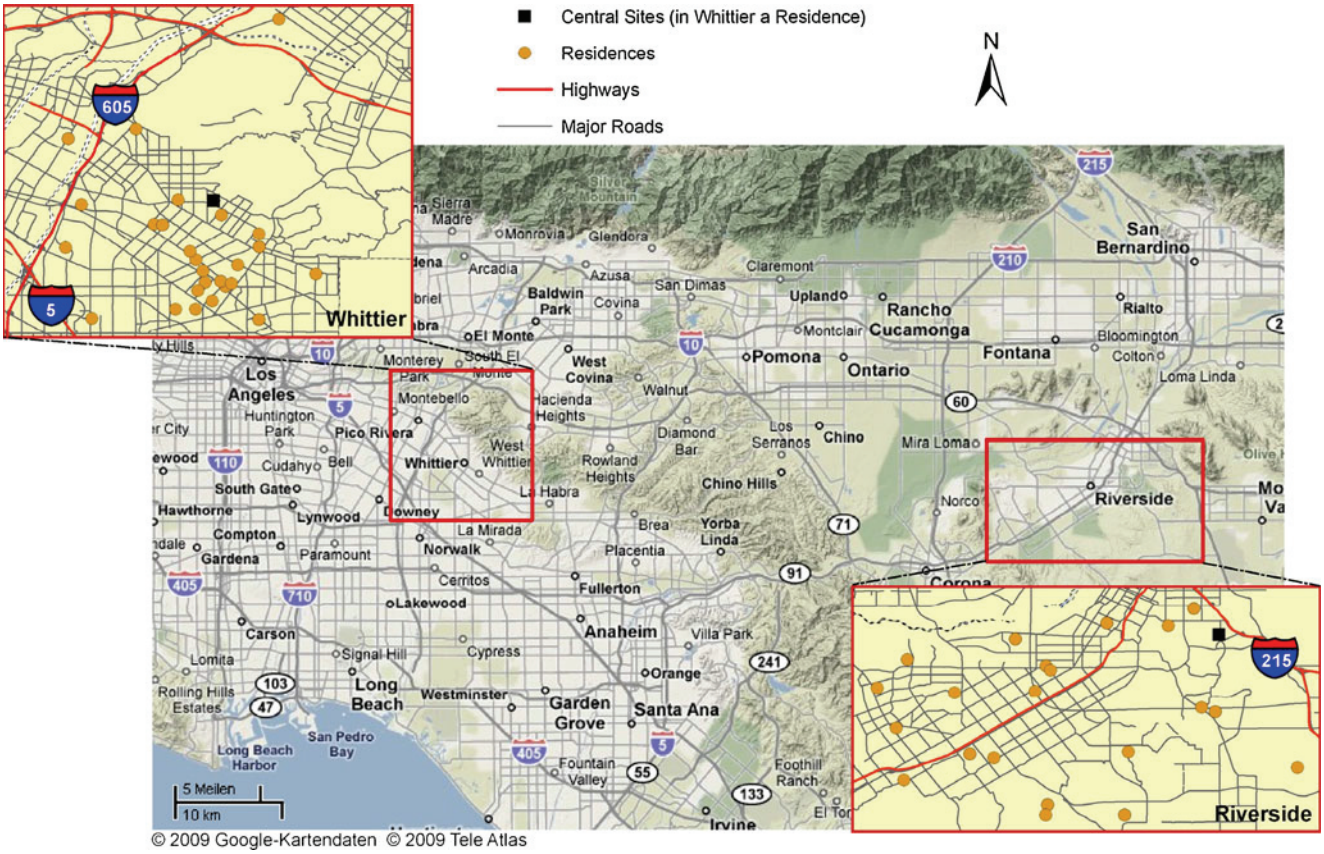


Fig. 1 Study area: Whittier and Riverside, in the Los Angeles air basin of Southern California. Detailed maps are not to scale

and central sites, 24-h $PM_{2.5}$ measurements were collected on Teflon and quartz filters using Harvard Impactors (Air Diagnostics and Engineering, Inc., Naples, ME, USA; Liu et al. 2003). Mass measurements were conducted with the Teflon filters using standard gravimetric methods. All quartz filters were analyzed for EC and OC using the thermal manganese dioxide oxidation protocol as with the personal filters (Fung et al. 2002).

Geocoding and traffic variables

Residences and schools were geocoded using the TeleAtlas Eagle Geocoding service (TeleAtlas, Redwood City, CA, USA). Annual average daily traffic count data in 2000 were obtained from the California Department of Transportation (Caltrans), assigned to TeleAtlas roadway links and adjusted to represent the years of 2003 and 2004 based on a statewide vehicle-miles-traveled growth, i.e., 2.4% per year from 2000 to 2004 (Wu et al. 2005b). Distance to different types of roadways (freeway, arterial, and collector roads) were calculated in ArcGIS 8.3 (ESRI, Redlands, CA, USA) based on TeleAtlas MultiNet™ USA roadway network. Traffic densities were calculated using the density plotting feature of ESRI Spatial Analyst software (ESRI, Redlands, CA, USA).

Dispersion model estimates

The CALINE4 dispersion model was used to predict traffic-specific pollutant concentrations ($PM_{2.5}$, EC, OC) for receptors given the source strength using emission factors, meteorology, and site geometry (Benson 1992). The uncertainties in EC and OC emission factors are discussed elsewhere (Wu et al. 2009). The original CALINE4 model was further modified to incorporate contributions from road segments within 5 km to a receptor (Wu et al. 2005c). Meteorological predictor variables were hourly wind speed, wind direction, and temperature which were taken from the Rubidoux SCAQMD site for Riverside and at the Pico Rivera SCAQMD site for Whittier, respectively. Also included in the predictions were average hourly mixing heights by season (cool and warm) which were obtained from the 1997 Southern California Ozone Study at the Los Angeles and Ontario International Airports for assignments to Whittier and Riverside, respectively (Croes and Fujita 2003).

Analysis

Summary characteristics and correlations were calculated for personal, home indoor, home outdoor, and central site

measurements by city. Separate and pooled mixed linear regression models with a random household effect were constructed for Riverside and Whittier to predict 24-h average home outdoor concentrations of $PM_{2.5}$, EC, and OC, respectively. The full model for each pollutant had the form:

$$C_{ij}^{\text{out}} = \beta_0 + \beta_1 \times C_j^{\text{Cn}} + \beta_2 \times C_{ij}^{\text{CAL}} + \beta_3 \times \text{city} + \sum_m \alpha_m \times traffic_{im} + \sum_n \delta_n \times G_{in} + \sum_p \gamma_p \times Met_{jp} + \sum_q \lambda_q \times \text{time}_{jq} + \varepsilon_{ij} \quad (1)$$

where C_{ij}^{out} and C_{ij}^{CAL} were the measured and CALINE4 modeled home outdoor pollutant concentrations, respectively, at home i on day j, and C_j^{Cn} represents central site measurements. City was an indicator variable in the pooled model. Three traffic variables (traffic_{im}, m=1–3) were used, including distance weighted traffic counts at the residence for heavy-duty vehicles, light-duty vehicles, and total traffic. The four geographical variables (G_{in}, n=1–4) included population density and minimal distance from the residence to roads of three different classes (highway (including freeways and other highways), arterial roads, and collector roads). Twelve meteorological variables (Met_{jp}, p=1–12) were tested including 24-h averages of temperature, relative humidity, season, wind speed, wind vectors, and wind direction frequencies. Wind vectors were calculated as the vector sum of hourly wind speeds and directions over a day with the resulting average wind directions categorized into four quadrants (N–E, E–S, S–W, and W–N). Wind direction frequencies were defined as hours per day from each of the four quadrants. Three time variables (time_{jq}, q=1–3) were included to account for daily or weekly cycles, including date_j, $\sin(t)$, and $\cos(t)$, where $t=2\pi \times \text{date}_j/7$. ε_{ij} described the model error.

In a first step, predictors were entered in the models using forward, backward, or stepwise selection procedures. Stepwise linear regression with a 0.1 significance level chosen for a covariate entering or staying in the model led to the best models. For the pooled models, a "city" effect was forced in if it was not retained during the selection process. In a second step, the important predictors that were determined from the above models were used in a mixed model with a random effect to account for data clustering within homes. The random effect fitted best when a compound symmetry correlation structure with heterogeneous variances between repeated measures was applied. Final models were selected based on model fit using the Akaike's information corrected criterion (AICC). We used the same modeling approach to predict the ratios of home outdoor to central site measurements that was used as a method to predict spatial variation. All models were examined for reliability using the "leave-one-out" cross-validation approach, where each observation was removed from the dataset and evaluated against the model prediction.

To examine the variation in personal exposure explained by the modeled home outdoor concentrations, adjusted R^2 from the linear regression and the bias (the differences between the measured and modeled values) are reported. Linear regression was also used to compare personal $PM_{2.5}$, EC, and OC measurements with the corresponding CALINE4 estimates at home. All statistical analyses were performed with SAS 9.1 (SAS Institute Inc., Cary, NC, USA).

Quality control

The data collection rate, defined as the number of valid samples divided by the total number of expected samples, for personal measurements of $PM_{2.5}$, EC, and OC ranged between 76% to 89% in Riverside and 94% to 95% in Whittier. For personal measurements in the 63 subjects, data from four Riverside subjects were excluded from analysis as the residences of two subjects (one with home monitoring) were outside the geographical area for the CALINE4 model and the other two subjects were not geocoded due to inadequate TeleAtlas data. Outdoor measurements from seven Riverside homes (excluding one above) and eight Whittier homes were pooled, totaling 131 $PM_{2.5}$ and 129 EC and OC measurements with matched central site measurements for modeling.

In Riverside, personal EC and OC data were excluded from analysis for the following reasons. We found poor correlations of personal EC and OC with indoor EC and OC (non-significant r values, 0.08 and 0.22, respectively). Despite the moderate correlations between personal and measured outdoor EC and OC in Riverside (r=0.35 and 0.45, respectively), the predicted outdoor concentrations from the home outdoor models did not describe the variation of the personal measurements for EC and OC (R^2=0.01 and 0.03, respectively). We attribute these results to a possible leakage problem in the filter cassettes at Riverside (cassettes were hand clamped not vise clamped). In addition, other unmeasured factors could have influenced these results, including those related to the community, differences in organic aerosol composition (described below) and thus OC sampling artifacts, or to between-subject differences in time-activity in Riverside vs. Whittier.

We also learned later that the pDRs used for Whittier subjects were calibrated by the manufacturer with different reference aerosols from those used for the Riverside pDRs, even though both were called "Arizona road dust". Furthermore, we expected a different aerosol composition in Whittier (more of a source site with higher primary combustion aerosols) vs. Riverside (more of a receptor site with higher secondary photochemical aerosols). To adjust

for this calibration difference, the personal pDR measurements were compared with the indoor Harvard Impactor measurements during the days when the subjects spent more than 98% of the time at home (additional Data given in Online Resource 1). While home indoor and personal measurements were about the same in Riverside (slope= 0.75), personal $PM_{2.5}$ measurements in Whittier had to be corrected according to following equation:

$$PM_{2.5,corr} = 0.317 \times PM_{2.5,meas} + 4.61$$

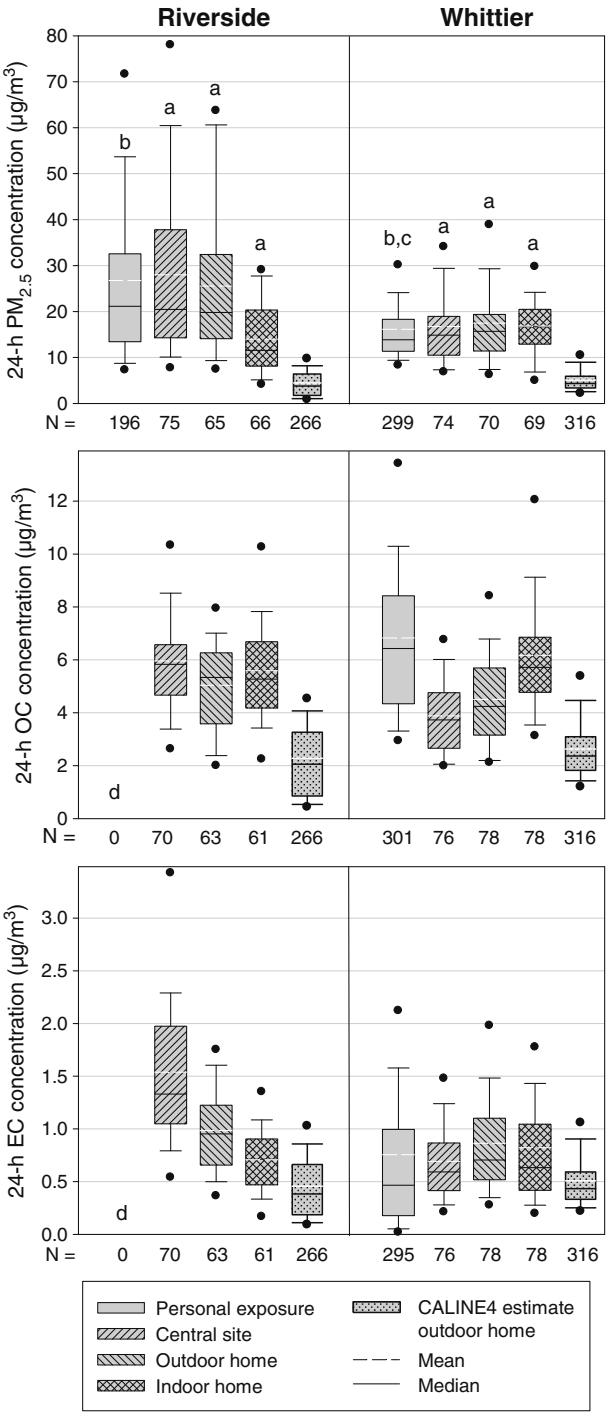
$$(N = 13, R^2 = 0.97) \quad (2)$$

The precision of the pDR was 5 μg/m^3 (Liu et al. 2002). The limit of detection (LOD), defined as three times the standard deviation of the field blanks, was 0.15 and 0.63 μg/m^3 for personal EC and OC in Whittier, respectively. The LOD for indoor, outdoor, and central site EC and OC measurements using the Harvard Impactors was 0.06 and 0.30 μg/m^3, respectively.

Results

Summary statistics

Outdoor $PM_{2.5}$ averaged 28.3 and 16.7 μg/m^3 in Riverside and Whittier, respectively. Personal $PM_{2.5}$ and outdoor EC and OC concentrations were also higher in Riverside than Whittier (Fig. 2). In Riverside, central site, personal, and home outdoor $PM_{2.5}$ concentrations were similar and about two times higher than the indoor concentrations. The low indoor concentrations might be explained by the more frequent use of air conditioning in Riverside compared to Whittier (42% vs. 34%). In Riverside, we also observed a difference between the homes with and without monitoring. Average pDR measurements when children were inside at home were lower in the group of children with home monitoring (20 μg/m^3 vs. 26 μg/m^3). For EC and OC in Riverside, central site levels were higher than home indoor and outdoor concentrations. In Whittier, $PM_{2.5}$ and EC levels were similar across all microenvironments, respectively, while OC levels were higher for personal and home indoor environments. The CALINE4 model estimates for $PM_{2.5}$, EC and OC from local mobile sources were expectedly lower than the actual measurements, which include all sources. Assuming CALINE4 estimates were accurate, then about 30% of outdoor $PM_{2.5}$ and 60% of EC and OC would have come from local traffic in Whittier, while in Riverside the local traffic contribution would only be 20% for $PM_{2.5}$ and 45% for EC and OC. This is in accordance with the GIS data (Table 1) showing that subjects in Whittier lived closer to major roads and were exposed to more traffic exhaust than subjects in Riverside.



[a] 24-h $PM_{2.5}$ collected with Harvard Impactors; [b] 24-h averages of 1-min pDR readings; [c] corrected $PM_{2.5}$; [d] Measurement error due to possible leaks in filter cassettes, data not used

Fig. 2 Daily averages of air pollution measurements by location

Correlation between personal, central site, and home measurements

Home outdoor concentrations of $PM_{2.5}$ were strongly correlated with those at the central sites (r=0.96–0.97)

Table 1 Daily averages of GIS parameters at subjects' homes

GIS variables	Riverside panel (27 subjects)				Whittier panel (32 subjects)			
	N	Mean (standard deviation)	Median	Min/ Max	*N*	Mean (standard deviation)	Median	Min/ Max
Population density (1/km^2)	266	1,712 (1,057)	1,696	141/3,782	316	3,568 (1,528)	2,952	978/6,575
Minimal distance to highways (m)	266	2,653 (1,933)	2,175	460/6,938	316	1,371 (929)	1,084	121/3,339
Minimal distance to arterial roads (m)	266	488 (537)	310	6/2,593	316	336 (317)	248	20/1,130
Minimal distance to collector roads (m)	266	492 (338)	401	26/1,275	316	294 (324)	144	4/1,238
Total traffic count (distance weighted)	266	404 (567)	228	68/3,149	316	617 (479)	545	125/2,207
Heavy-duty vehicle traffic count (distance weighted)	266	21 (18)	12	5/75	316	23 (18)	16	5/89
Light-duty vehicle traffic count (distance weighted)	266	384 (562)	216	63/3,074	316	594 (464)	521	116/2,147

and less so with the home indoor measurements (r=0.48–0.79) (Table 2). Likewise, personal $PM_{2.5}$ measurements showed good correlations with those at the central (r=0.81–0.84) and home outdoor (r=0.77–0.88) sites and less so with those at home indoor sites (r=0.65–0.85). Compared to $PM_{2.5}$, slightly weaker correlations were found between home outdoor and central site measurements of OC (r=0.78–0.86) and EC (r=0.68–0.89). Correlations for OC and EC between indoor and outdoor measurements were weaker in Riverside (r=0.41 and 0.49, respectively) than in Whittier (r=0.72 and 0.63). In Whittier, correlations between personal and central site OC and EC were low (r=0.22 and 0.29, respectively) and correlations between personal and outdoor site OC and EC were moderate (r=0.55 and 0.57, respectively). Personal EC concentrations showed a strong correlation with home indoor EC (r=0.90) and personal OC showed a moderate correlation with indoor OC (0.54).

As the CALINE4 model estimated air pollution exposures driven by local traffic exhaust alone, evaluation of these estimates is not straightforward because our ambient measurements include both local and regional pollution. Thus, we compared CALINE4 estimates to home outdoor and personal EC measurements, which were assumed to better represent local traffic sources than OC or $PM_{2.5}$. In Riverside, the correlation between measured EC and estimated CALINE4 EC for the home outdoor environment was not significant. In Whittier, CALINE4 home outdoor EC estimates showed a moderate correlation to home outdoor EC measurements (r=0.51), while little correlation was found with personal exposure to EC, even after excluding subjects who reported indoor sources (r=0.18, without outliers).

Home outdoor models

The best models from the stepwise regression for home outdoor $PM_{2.5}$, OC, and EC for individual cities and pooled data are shown in Table 3. The central site measurement was the predominant predictor in all models, accounting for more than 93%, 61%, and 46% of the variability in home outdoor $PM_{2.5}$, OC, and EC concentrations, respectively. For $PM_{2.5}$, the adjusted R^2 was over 0.94 in models for Riverside, Whittier, and the pooled data. For OC models, the adjusted R^2 was 0.91 for Riverside, 0.83 for Whittier, and 0.80 for the pooled model. The second most important predictors in the OC models included minimal distance to collector roads for Riverside (partial R^2=0.14) and temperature for Whittier (partial R^2=0.16). For EC models, the adjusted R^2 was 0.76 for Riverside, 0.87 for Whittier, and 0.75 for the pooled model. The second most important predictors in the EC models included minimum distance to

Table 2 Pearson correlations between the concentrations at different locations by pollutant

		Riverside			Whittier			Pooled		
		Central Site	Home outdoor	Home indoor	Central Site	Home outdoor	Home indoor	Central Site	Home outdoor	Home indoor
$PM_{2.5}$	Home outdoor	0.97		0.79	0.96		0.48	0.97		0.57
	Personal	0.81	0.88	0.85	0.83	0.77	0.74	0.84	0.86	0.65
OC	Home outdoor	0.86		0.41	0.78		0.72	0.79		0.56
	Personal	N/A	N/A	N/A	0.22	0.55	0.54	N/A	N/A	N/A
EC	Home outdoor	0.68		0.49	0.89		0.63	0.70		0.55
	Personal	N/A	N/A	N/A	0.29	0.57	0.90	N/A	N/A	N/A

All correlations were significant with p<0.01

highway for Riverside (partial R^2=0.19) and wind direction for Whittier (partial R^2=0.06). Both OC and EC models with pooled data identified population density as the second most important predictor. While wind variables were significant in all EC and OC models, CALINE4 estimates only entered the EC model for Whittier.

Since the central site measurements accounted for most of the temporal variation, we also tested models for the prediction of ratios of home outdoor to central site measurements by the same variables tested above. This was intended to reduce the temporal variation across raw measurements that were taken at different times (different 10-day runs) and to examine predictors of spatial variation. Results in Table 4 suggest that spatial variation was only a fraction of the total variation in the measurements because all ratio models had lower R^2 values than the concentration models (Table 3). The EC ratio model for Whittier had the lowest R^2 suggesting lower spatial variability in EC (Table 4). Given the higher R^2 values, we used the concentration models in the following section for evaluation of the representativeness of predicted outdoor home to personal exposure measurements.

Figures 3 and 4 provide a visual display of model performance. These figures plot 10-day averaged ratios of home outdoor to central site OC as well as EC, using actual measurements (Fig. 3a, b for Whittier and Fig. 4a, b for Riverside) as well as model predictions using equations developed from Table 3 models (Fig. 3c–f for Whittier and Fig. 4c–f for Riverside). We used two types of models, one was specific to the city (Figs. 3c, d and 4c, d), the other was the model using data from both cities (pooled model) and applied for predictions in the specific city (Figs. 3e, f and 4e, f). In Whittier, air pollution concentrations were lower at the central site than those at outdoor home sites, resulting in ratios mostly above 1. In contrast, the higher concentrations at the Riverside central site, located 600 m from the 215 freeway, resulted in lower ratios. In Whittier, no spatial patterns could be observed for either measured (Fig. 3a) or estimated OC ratios (Fig. 3c and e), whereas in Riverside, both measured (Fig. 4a) and estimated OC ratios (Fig. 4c and e) were higher along freeways and in areas with a denser street network. For EC, plots based on actual measurements showed higher ratios along freeways in both cities (Figs. 3b and 4b), which were captured by the city-specific models (Figs. 3d and 4d). In Whittier, however, the freeway effect disappeared in the pooled model predictions (Figs. 3f).

Comparisons between personal and predicted outdoor exposures

Estimates from the home outdoor $PM_{2.5}$ models explained 65%, 69%, and 69% of the variation in personal $PM_{2.5}$ measurements in Riverside, in Whittier, and both cities pooled, respectively (Fig. 5a). The prediction bias, expressed as the difference between measured and predicted values was below 1 μg/m^3 for all models. There was no difference in the performance between the city-specific and the pooled model predictions (Fig. 5a and b, respectively). Estimated outdoor $PM_{2.5}$ explained more variation in personal $PM_{2.5}$ exposure among individuals with monitored homes than those without monitored homes (Fig. 5c).

Comparisons between personal and estimated outdoor OC and EC data were performed for Whittier only, as the personal EC and OC data in Riverside were removed after quality control. Predictions from the home outdoor OC model explained little of the variation in personal OC exposure (R^2=0.05). Exclusion of three unexplained high OC measurements (>3 SD from the mean and identified with arrows in Fig. 6) increased the model fit slightly to 0.08, with a prediction bias of 2.3 μg/m^3, about 35% of the mean (6.6 μg/m^3). Outdoor OC estimates at monitored homes explained only a slightly higher percentage of the variability in measured personal OC as compared with those at the non-monitored homes (Fig. 6).

Similarly, home outdoor EC estimates explained a small percentage of the variation in personal EC measurements (R^2=0.1). However, exclusion of four outliers (>3 SD from the mean) due to candle burning and cooking increased the R^2 to 0.37 (Fig. 7). The prediction bias was −0.2 μg/m^3, which is 33% of the mean (0.6 μg/m^3). The EC model predicted slightly better for the subjects with home measurements.

Effects of PM sources

We further examined these outdoor predictions by removing measurements with self-reported indoor sources (near smoking or cooking), defined when there was at least one 15-min entry of any indoor pollution event in the time-activity diary during each run day. The percentage of pollution events was similar in both cities, 42 of 266 in Riverside and 62 of 316 subject-days in Whittier. No significant differences in the performance of model predictions were found for all $PM_{2.5}$, OC, and EC models between the groups with or without reported indoor sources.

Seasonal effects

As the measurements were taken in two different seasons in each city, we looked for differences in model performance by season. For $PM_{2.5}$ the correlations between measured personal exposure and predicted home outdoor concentrations showed no significant difference between summer

Table 3 Results of linear regression modeling for home outdoor measurements of $PM_{2.5}$, OC, and EC

Dependent variable *Model*	*N*	Predictor Variable	Estimate	SE	Partial R^2	Adj. Model R^2
Home $PM_{2.5}$ ($\mu g/m^3$)						
Riverside	62	Central site $PM_{2.5}$ measurement ($\mu g/m^3$)	0.77**	0.02	0.96	0.97
		Relative humidity at central site (%)	0.07**	0.03	0.01	
		Heavy-duty vehicle traffic count (distance weighted)	0.10**	0.03	0.01	
		Weekly time term (sin)	1.09*	0.54	2.0E-03	
Whittier	69	Central site $PM_{2.5}$ measurement ($\mu g/m^3$)	0.97**	0.03	0.93	0.94
		Average wind speed (miles/h)	−0.89	0.62	4.9E-03	
		Weekly time term (sin)	0.95*	0.45	4.0E-03	
		Frequency of wind direction from N to E	0.12	0.08	3.3E-03	
Pooled	131	Central site $PM_{2.5}$ measurement ($\mu g/m^3$)	0.83**	0.02	0.94	0.96
		Minimal distance to highway (m)	−7.4E-04**	1.8E-04	0.01	
		City	−0.14	0.67	0.01	
		Total traffic count (distance weighted)	2.1E-03*	8.0E-04	2.6E-03	
		Weekly time term (sin)	1.00**	0.37	2.5E-03	
		Average temperature at central site (°F)	−0.09**	0.03	2.2E-03	
		Average wind speed (miles/h)	−0.65	0.34	1.0E-03	
Home OC ($\mu g/m^3$)						
Riverside	55	Central site OC measurement ($\mu g/m^3$)	0.65**	0.04	0.74	0.91
		Minimal distance to collector road (m)	1.5E-03**	2.0E-04	0.14	
		Weekly time term (sin)	0.40**	0.12	0.02	
		Average wind direction from N to E	0.85**	0.30	0.01	
		Relative humidity at central site (%)	0.02**	4.7E-03	0.01	
Whittier	75	Central site OC measurement ($\mu g/m^3$)	1.13**	0.07	0.61	0.83
		Average temperature at central site (°F)	−0.11**	0.02	0.16	
		Average wind direction from W to N	1.27**	0.40	0.03	
		Average wind speed (miles/h)	−0.59**	0.18	0.02	
		Weekly time term (cos)	−0.40**	0.13	0.02	
		Minimal distance to highway (m)	−3.7E-04	2.2E-04	3.4E-04	
Pooled	130	Central site OC measurement ($\mu g/m^3$)	0.77**	0.05	0.62	0.80
		Population density (per km^2)	2.7E-04**	7.6E-05	0.12	
		Average wind direction from W to N	0.59*	0.27	0.02	
		Relative humidity at central site (%)	9.9E-03	5.9E-03	0.02	
		Minimal distance to highway (m)	−1.7E-04**	5.6E-05	0.01	
		City	0.37	0.44	0.01	
		Frequency of wind direction from E to S	−0.10**	0.03	0.01	
		Frequency of wind direction from S to W	−0.04	0.02	0.01	
		Average wind speed (miles/h)	−0.28*	0.12	0.01	
		Average wind direction from E to S	0.63	0.33	1.3E-03	
Home EC ($\mu g/m^3$)						
Riverside	55	Central site EC measurement ($\mu g/m^3$)	0.49**	0.05	0.46	0.76
		Minimal distance to highway (m)	−6.9E-05**	1.5E-05	0.19	
		Average wind direction from N to E	−0.48**	0.11	0.05	
		Average wind direction from E to S	−0.40*	0.16	0.03	
		Average wind speed (miles/h)	0.10*	0.04	0.02	
		Daily time term (sin)	−0.09*	0.04	0.02	
Whittier	75	Central site EC measurement ($\mu g/m^3$)	0.93**	0.06	0.79	0.87
		Frequency of wind direction from N to E	0.03**	4.9E-03	0.06	
		EC CALINE4 home estimates	0.38**	0.12	0.02	

Table 3 (continued)

Dependent variable *Model*	*N*	Predictor Variable	Estimate	SE	Partial R^2	Adj. Model R^2
Pooled	130	Central site EC measurement (μg/m^3)	0.66**	0.04	0.48	0.75
		Population density (per km^2)	6.6E-05**	2.1E-05	0.16	
		Minimal distance to highway (m)	−6.1E-05**	1.6E-05	0.04	
		Relative humidity at central site (%)	3.8E-03*	1.8E-03	0.03	
		Frequency of wind direction from E to S	−0.04**	8.2E-03	0.02	
		Frequency of wind direction from S to W	−0.02**	6.7E-03	0.02	
		Average wind direction from N to E	−0.24*	0.10	0.01	
		City	0.17	0.13	1.2E-04	

SE standard error

*$p<0.05$; **$p<0.01$

and winter ($R^2=0.69$ and $R^2=0.62$, respectively). However, in Whittier home outdoor models for EC and OC explained more of the personal exposure variance in winter than in summer (EC: $R^2=0.56$ and 0.30, OC: $R^2=0.22$ and 0.09, respectively).

Discussion

In contrast to a previous validation study (Nethery et al. 2008), we found that predictions for daily concentrations of $PM_{2.5}$ in the outdoor home model were good surrogates for personal exposure to $PM_{2.5}$. Since local traffic accounted for less than 30% of the $PM_{2.5}$ measurements in our study cities, the remarkable performance of the $PM_{2.5}$ models likely reflected the common sources of regional transported $PM_{2.5}$ contributing to both the personal and outdoor $PM_{2.5}$. Home outdoor prediction models for specific components of $PM_{2.5}$ (EC and OC) were poorer indicators of personal exposure probably because these exposures are more affected by local sources such as traffic. Therefore, home outdoor models may not be adequate for predicting personal short-term exposure to specific sources that are relevant to studies of acute health outcomes. This conclusion most likely does not apply to the prediction of long-term exposures in studies of chronic health outcomes because it is expected that a smoothing of daily exposure variation would lead to less error in the prediction. This issue could not be addressed in the present study because we only collected ten consecutive days of sampling per subject.

We found strong correlations between personal and indoor EC but weaker correlations with outdoor and central site EC. Similar correlations were reported for EC during the summer in Boston, MA, USA (Brown et al. 2008) and for black smoke in Gothenburg, Sweden (Johannesson et al. 2007). The EC models showed comparable spatial patterns and predictors between our study cities. Clougherty et al. (2008) reported similar predictor variables which were important for personal EC and NO_2 models during the summer in Boston. Ryan et al. (2008) showed an improvement by 0.02 for the model R^2 of an outdoor model for traffic-related EC when adding wind parameters to the model in addition to traffic parameters. In our models, wind parameters showed similar effects with partial R^2 between 0.01 and 0.06. The lack of predictive power of the home outdoor EC models for personal EC exposure in the present study could be explained by the moderate correlations between personal and actual outdoor EC measurements ($r=0.57$ in Whittier). A better approach to predicting personal exposure to EC would entail the combination of a better model to predict home outdoor EC and knowledge of other sources of personal EC exposure linked to personal activities. Measurement errors in personal EC exposure might also contribute to part of the poor prediction.

This was the first study that examined the spatial variation of OC and predictors of personal OC exposure. Major predictors for the spatial variation of outdoor home OC varied depending on the study area (based on our ratio models for home outdoor to central site OC measurements). In Riverside, the major predictor was the heavy-duty vehicle counts, while in Whittier it was temperature. When data were pooled, the minimal distance to collector roads was the most important predictor, likely because this variable provided a local source contrast between these two cities. Wind variables played a minor role in all ratio models, likely accounting for some of the upwind/down-wind influences of OC sources.

Although the R^2 values of our home outdoor OC models were above 0.8, these models provided poor estimates for personal OC exposure. The weak personal–central site correlations of OC measurements also indicated sources other than regional PM contributing to personal OC exposure. Nevertheless, OC measurement error might also

Table 4 Results of linear regression modeling for ratios of home outdoor to central site measurements of $PM_{2.5}$, OC, and EC

Dependent variable *Model*	*N*	Predictor variable	Estimate	SE	Partial R^2	Adj. model R^2
$PM_{2.5}$ ratio						
Riverside	62	Population density (per km^2)	1.7E-04**	2.7E-05	0.36	0.43
		Relative humidity at central site (%)	4.3E-03**	1.1E-03	0.07	
		Average wind direction from N to E	0.12	0.07	0.03	
Whittier	69	Frequency of wind direction from N to E	0.02**	0.01	0.24	0.31
		Weekly time term (cos)	−0.09**	0.03	0.08	
		Average wind direction from W to N	0.20	0.11	0.02	
Pooled	131	Minimal distance to highway (m)	−5.3E-05**	1.1E-05	0.24	0.38
		Frequency of wind direction from N to E	0.02**	4.8E-03	0.06	
		Average temperature at central site (°F)	−0.01*	2.1E-03	0.05	
		Weekly time term (cos)	−0.08**	0.03	0.05	
		city	0.04	0.07	2.0E-03	
		Average wind direction from W to N	0.10	0.05	5.4E-05	
OC ratio						
Riverside	55	Heavy-duty vehicle traffic count (distance weighted)	0.01**	1.2E-03	0.47	0.70
		Relative humidity at central site (%)	3.3E-03**	9.0E-04	0.09	
		Average wind speed (miles/h)	0.09**	0.02	0.09	
		Weekly time term (sin)	0.05*	0.02	0.03	
		Frequency of wind direction from N to E	0.02*	0.01	0.02	
		Average wind direction from N to E	−0.26**	0.07	0.02	
Whittier	75	Average temperature at central site (°F)	−0.02**	4.1E-03	0.45	0.58
		Average wind direction from W to N	0.35**	0.11	0.07	
		Weekly time term (cos)	−0.12**	0.03	0.06	
		Average wind speed (miles/h)	−0.10*	0.04	0.02	
		Heavy-duty vehicle traffic count (distance weighted)	3.3E-03	1.7E-03	0.01	
Pooled	75	Minimal distance to collector road (m)	−4.2E-04**	6.4E-05	0.24	0.63
		city	−0.03	0.05	0.17	
		Frequency of wind direction from N to E	0.04**	0.01	0.08	
		Average temperature at central site (°F)	−0.01*	3.4E-03	0.06	
		Relative humidity at central site (%)	4.9E-03*	1.9E-03	0.04	
		Weekly time term (cos)	−0.08**	0.02	0.03	
		Daily time term (sin)	−0.05*	0.02	0.01	
		Average wind direction from N to E	−0.34**	0.08	0.01	
EC ratio						
Riverside	55	Relative humidity at central site (%)	0.01**	1.5E-03	0.34	0.66
		Minimal distance to highway (m)	−5.6E-05**	9.5E-06	0.24	
		Weekly time term (sin)	0.07*	0.03	0.04	
		Average temperature at central site (°F)	0.01	0.03	0.03	
		Average wind speed (miles/h)	0.07*	0.03	0.03	
		Average wind direction from S to W	0.14*	0.03	0.02	
Whittier	75	Ratio of EC CALINE4 home/central site estimates	0.24**	0.07	0.14	0.31
		Average temperature at central site (°F)	−0.03**	0.01	0.14	
		Average wind direction from N to E	−0.61*	0.27	0.04	
		Weekly time term (cos)	−0.12	0.07	0.03	
Pooled	130	Ratio of EC CALINE4 home/central site estimates	0.22**	0.08	0.41	0.53
		Population density (per km^2)	−4.1E-06	4.3E-05	0.04	
		Frequency of wind direction from N to E	0.03*	0.01	0.04	
		Weekly time term (sin)	0.11*	0.05	0.02	
		Daily time term (sin)	−0.08	0.04	0.02	
		Frequency of wind direction from S to W	−0.02	0.01	0.01	
		Average wind speed (miles/h)	0.12*	0.05	0.01	
		Average wind direction from N to E	−0.52**	0.16	0.01	
		City	0.32*	0.15	4.1E-03	

SE standard error

*$p<0.05$; **$p<0.01$

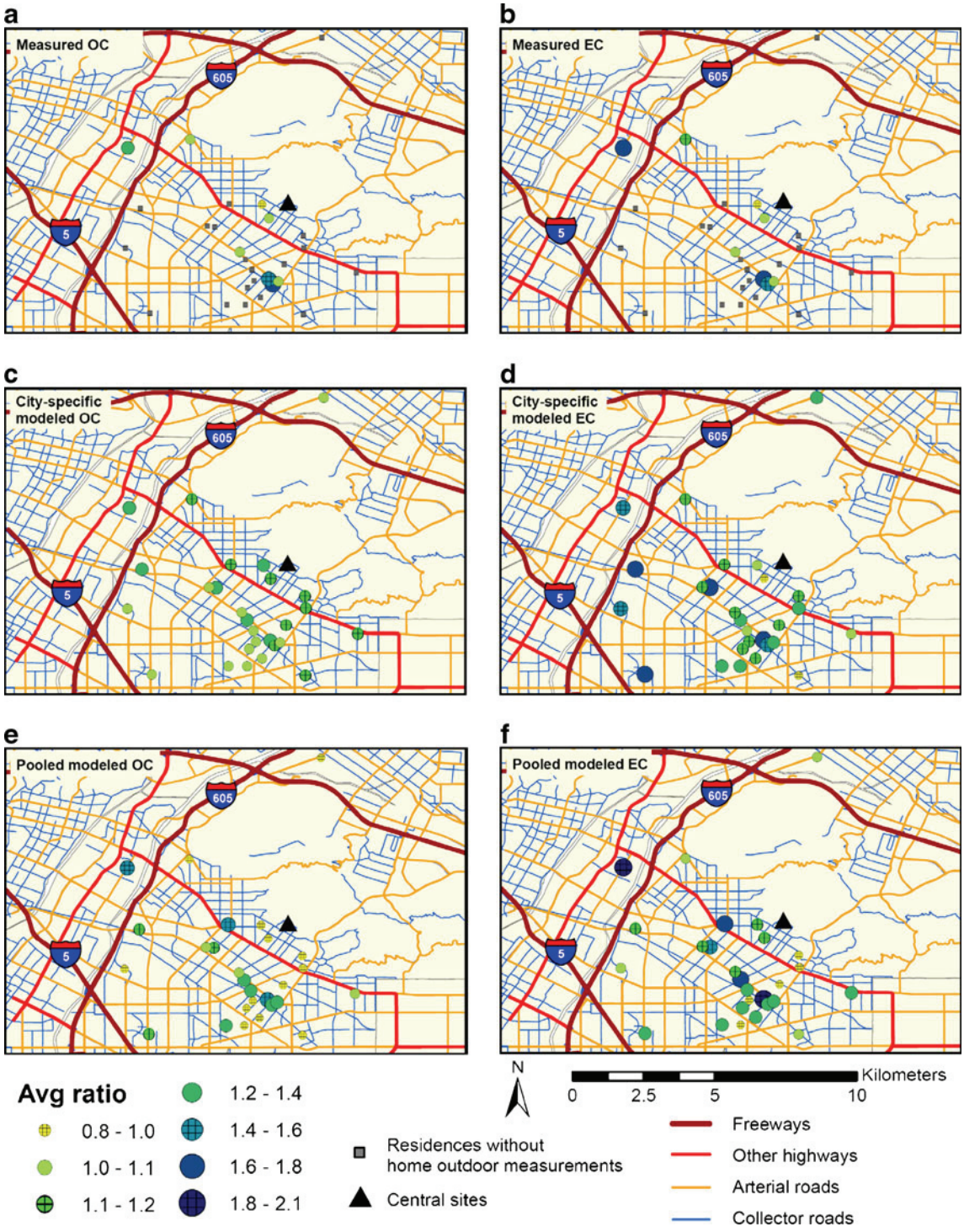


Fig. 3 Plots of 10-day average ratios of home outdoor to central site OC (*left panel*) and EC (*right panel*) levels in Whittier, using measurements (**a** and **b**), city-specific model predictions (**c** and **d**), and pooled model predictions (**e** and **f**)

contribute to part of the poor prediction of personal exposure (which was possible for the Riverside data we omitted). Previous studies have reported OC sampling artifacts due to the OC adsorption onto quartz filters, especially for OCs with lower molecular weights (Kirchstetter et al. 2001; Olson and Norris 2005; Turpin et al. 1994, 2000). This positive artifact could become profound for indoor measurements due to more abundant OC sources indoors than outdoors (Landis et al. 2001; Long et al. 2000; Pang et al. 2002). As our study did not implement back-up quartz filters to correct for the sampling artifact, personal OC measurements could be overestimated (Fig. 6).

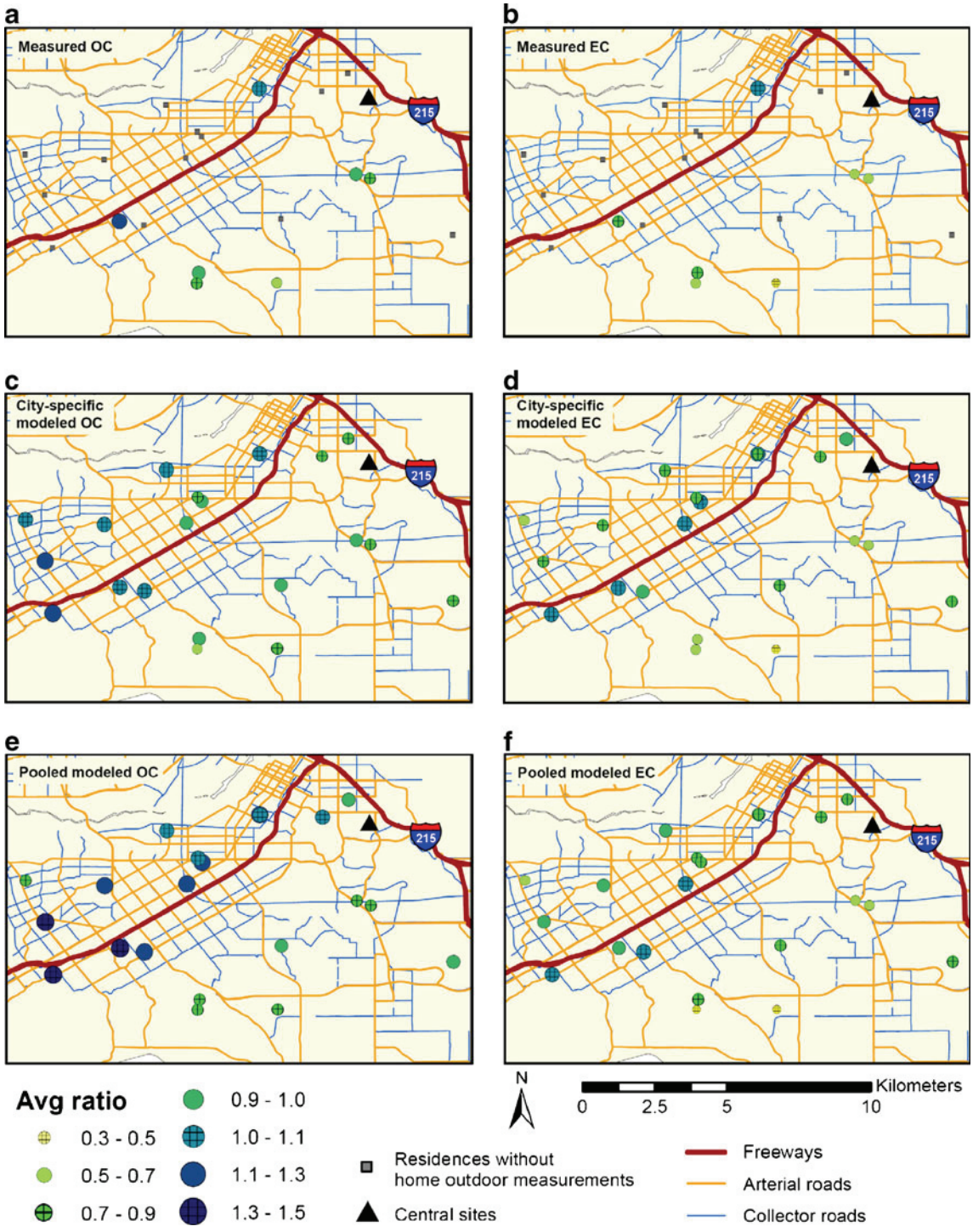


Fig. 4 Plots of 10-day average ratios of home outdoor to central site OC (*left panel*) and EC (*right panel*) levels in Riverside, using measurements (**a** and **b**), city-specific model predictions (**c** and **d**), and pooled model predictions (**e** and **f**)

The CALINE4 model, which takes into account source strengths and atmospheric convection processes, has been used by previous studies to estimate traffic-specific outdoor exposure in chronic health effect assessment (Gauderman et al. 2005; Molitor et al. 2006, 2007). In our stepwise regression modeling, the CALINE4 estimates only entered the models in Whittier for the prediction of home outdoor EC. It is likely that seasonal averages of meteorological parameters and annual traffic counts that were used in the CALINE4 model predictions could not capture the finer temporal variation in our daily measurements. The CALINE4 estimates also suffered from missing heavy-duty truck counts for some

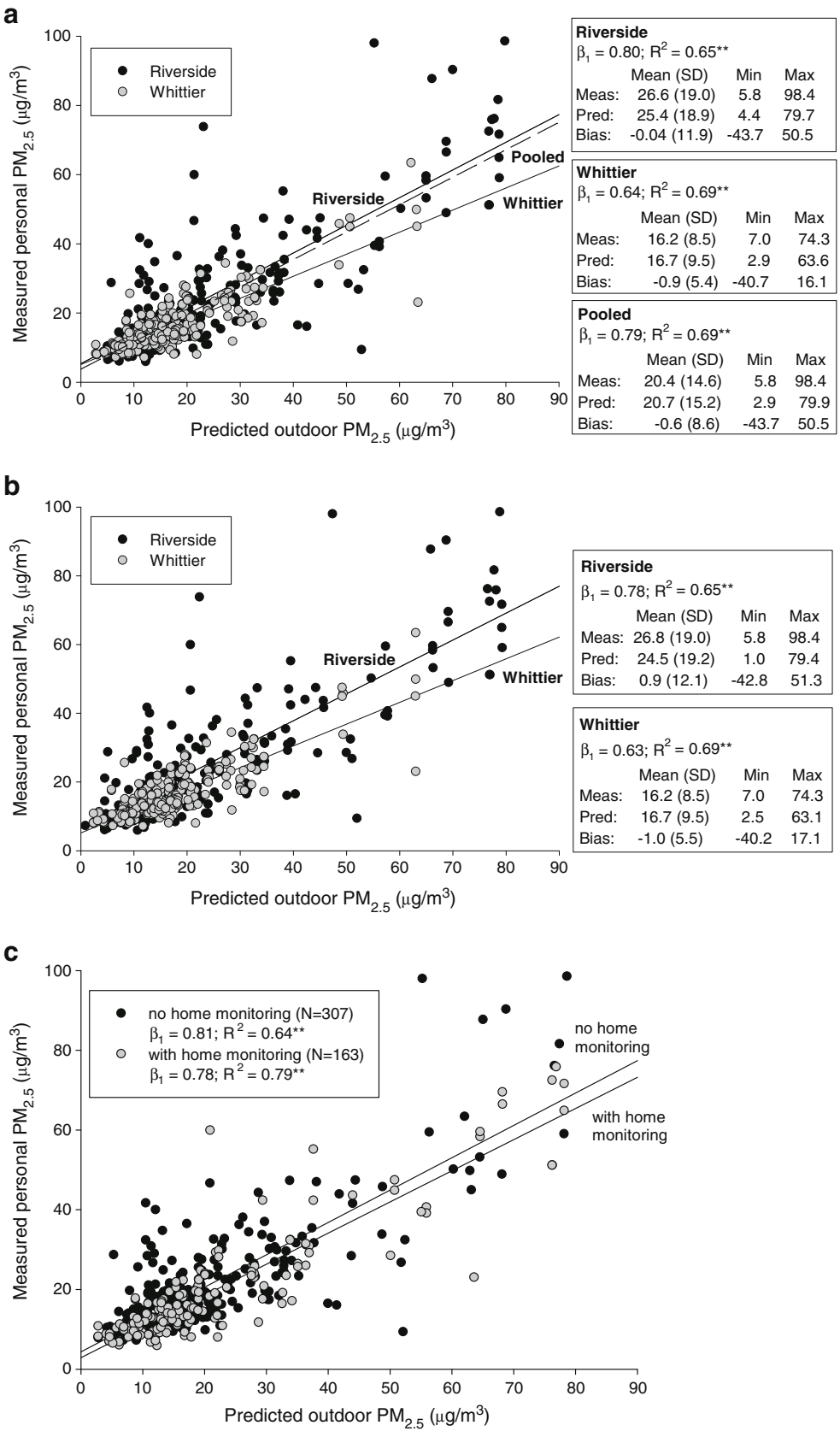


Fig. 5 Relationship between measured personal $PM_{2.5}$ and predicted home outdoor $PM_{2.5}$ from concentration models with a random "home" effect using **a** a pooled model, **b** city-specific models, and **c** grouped by monitored homes from the pooled model (β_1=estimate of regression slope; $^{**}p<0.01$). Statistics for measured (*Meas*) and predicted (*Pred*) $PM_{2.5}$ and the *Bias* are provided in *text boxes*

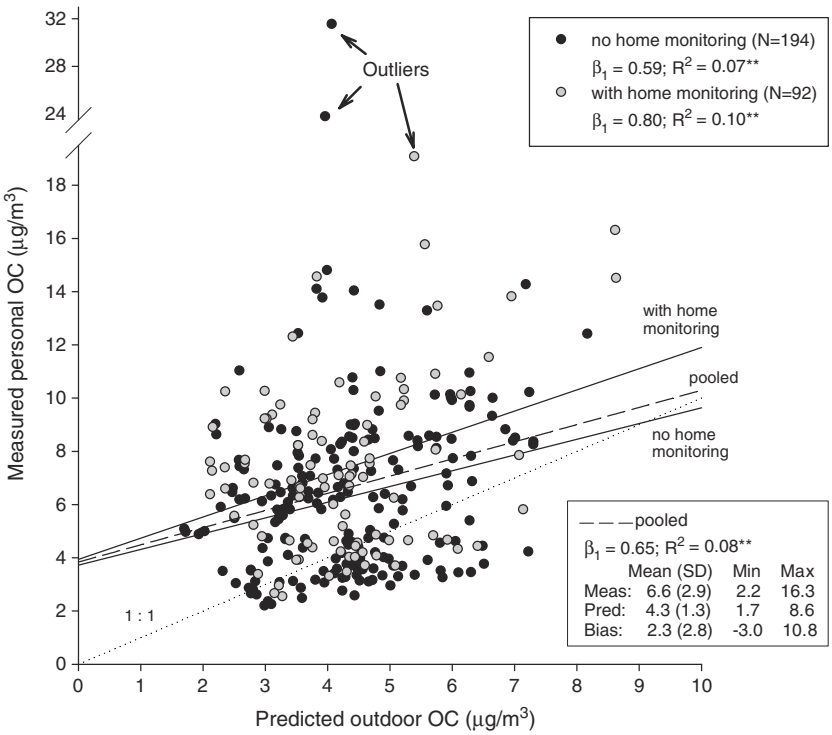


Fig. 6 Relationship between measured personal OC vs. predicted home outdoor OC from the city-specific concentration model for Whittier with a random "household" effect. All statistics were calculated without the three outliers (**$p<0.01$)

roadways in our study areas. Furthermore, no validation study has been conducted to our knowledge to verify the emission factors we used for EC and OC species in the CALINE models. Additionally, home outdoor EC estimates from CALINE4 had a moderate correlation with home outdoor EC measurements and a low correlation with personal EC measurements, which consisted of exposures in various other microenvironments. Therefore, it remains unclear whether studies of health responses to acute exposures should use CALINE4 predictions of outdoor home EC to represent personal exposure to traffic. Studies with more specific traffic markers (e.g., 1-nitropyrene for diesel exhaust) or source apportioned traffic estimates are needed to further evaluate the CALINE4 estimates.

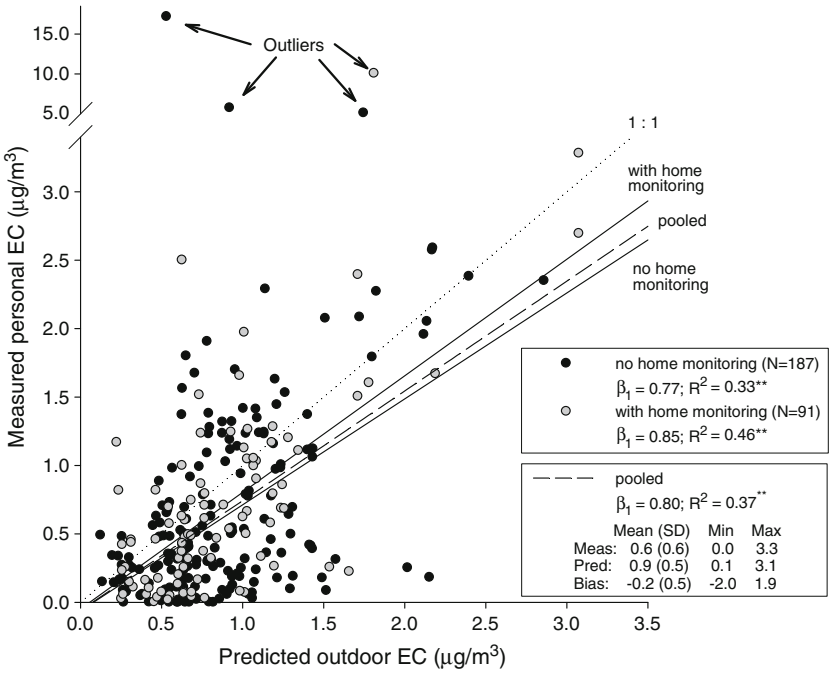


Fig. 7 Relationship between measured personal EC vs. predicted home outdoor EC from the city-specific concentration model for Whittier with a random "household" effect. All statistics were calculated without the four outliers (**$p<0.01$)

The ratio plots (Figs. 3 and 4) demonstrated spatial variation of EC and OC. While measured and predicted (city-specific) EC showed clear freeway effects, OC was more homogeneously distributed with higher ratios in areas with a denser street network. The lack of a freeway influence on OC was likely due to the minor influence of traffic sources, which is in accordance with a study in Mira Loma, close to Riverside (Na et al. 2004). In addition, the limited number of monitored homes might have not adequately covered the entire geographic range. The pooled models resulted in smoothed spatial variation near freeways, especially for EC. In summary, city-specific models captured more spatial variation than the pooled models.

In our study, personal–outdoor correlations for $PM_{2.5}$ were higher than personal–indoor correlations, and home outdoor concentrations were highly related to the central site measurements. Although most studies have found higher personal–indoor correlations than personal–outdoor correlations (Crist et al. 2008; Delfino et al. 2004; Liu et al. 2003; Meng et al. 2005), Brown et al. (2008) reported results similar to ours. The predominant predictor for all home outdoor models was the central site measurements, and these modeled outdoor levels, in turn, predicted short-term personal $PM_{2.5}$ exposure well. The ability to predict personal $PM_{2.5}$ did not differ by models (city-specific vs. pooled). Our results reinforced the earlier findings about the spatial homogeneity of outdoor $PM_{2.5}$ in an air shed (Krudysz et al. 2008) due to the major contribution from regional sources.

Although season was never retained as a significant predictor variable in the home outdoor models, we found seasonal differences in the ability to predict personal EC and OC but not for $PM_{2.5}$. In winter, air stagnation episodes with lower mixing heights lead to increased concentrations of traffic-related carbonaceous aerosols at ground level. This is expected to lead to increased indoor infiltration. On the other hand, $PM_{2.5}$ has a variable mixture of components across seasons, with more secondary aerosols in the summer, including nitrates.

As subjects spent most of their time indoors, we expected that the influence of indoor sources on personal exposure would diminish the predictability of the home outdoor models. However, this was not true for any of the pollutants due in part to the small number of reported incidences of indoor source exposures (mostly over brief periods). Similar results were found by Van Roosbroeck et al. (2008) who showed no effect of indoor sources on personal soot exposures.

Conclusions

We demonstrated that home outdoor models could be constructed with excellent predictions of daily $PM_{2.5}$, OC, and EC concentrations and using a limited number of monitoring sites within a city. Due to different predictive parameters of the EC and OC spatial pattern between Riverside and Whittier, city-specific models performed better than the pooled models. This suggests that future studies should take subregional differences into account for predicting outdoor spatial variation of EC and OC. We found that daily personal $PM_{2.5}$ exposure correlated well with the predicted home outdoor $PM_{2.5}$ concentrations. However, daily personal EC or OC exposure were poorly approximated by home outdoor EC or OC estimates. Results of our personal exposure analysis may not be generalized to other population groups, e.g., adults, as children with asthma probably have different activity patterns. Future work to predict short-term exposure to traffic-related particulate air pollution should focus on building personal exposure models that incorporate information on personal activities, locations, and highly specific measurements of traffic markers.

Acknowledgments The study was supported by the National Institute of Environmental Health Sciences (ES11615) of the U.S. National Institutes of Health (NIH), and partially by a training grant at the Institute of Social and Preventive Medicine at the University of Basel, Switzerland (RD-S). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIH. The authors declare they have no competing financial interests.

References

Benson PE (1992) A review of the development and application of the CALINE3 and 4 models. Atmos Environ B Urban Atmos 26 (3):379–390

Brown KW, Sarnat JA, Suh HH, Coull BA, Spengler JD, Koutrakis P (2008) Ambient site, home outdoor and home indoor particulate concentrations as proxies of personal exposures. J Environ Monit 10(9):1041–1051

Brunekreef B, Holgate ST (2002) Air pollution and health. Lancet 360 (9341):1233–1242

Chakrabarti B, Fine PM, Delfino R, Sioutas C (2004) Performance evaluation of the active-flow personal DataRAM PM2.5 mass monitor (Thermo Anderson pDR-1200) designed for continuous personal exposure measurements. Atmos Environ 38(20):3329–3340

Clougherty J, Wright R, Baxter L, Levy J (2008) Land use regression modeling of intra-urban residential variability in multiple traffic-related air pollutants. Environ Health 7(1):17

Crist KC, Liu B, Kim M, Deshpande SR, John K (2008) Characterization of fine particulate matter in Ohio: indoor, outdoor, and personal exposures. Environ Res 106(1):62–71

Croes BE, Fujita EM (2003) Overview of the 1997 Southern California Ozone Study (SCOS97-NARSTO). Atmos Environ 37(S2):S3–S26

Delfino RJ, Quintana PJ, Floro J, Gastanaga VM, Samimi BS, Kleinman MT, Liu LJ, Bufalino C, Wu CF, McLaren CE (2004)

Association of FEV1 in asthmatic children with personal and microenvironmental exposure to airborne particulate matter. Environ Health Perspect 112(8):932–941

Delfino RJ, Staimer N, Gillen D, Tjoa T, Sioutas C, Fung K, George SC, Kleinman MT (2006) Personal and ambient air pollution is associated with increased exhaled nitric oxide in children with asthma. Environ Health Perspect 114(11):1736–1743

Delfino RJ, Staimer N, Tjoa T, Gillen D, Kleinman MT, Sioutas C, Cooper D (2008) Personal and ambient air pollution exposures and lung function decrements in children with asthma. Environ Health Perspect 116(4):550–558

Delfino RJ, Chang J, Wu J, Ren C, Tjoa T, Nickerson B, Cooper D, Gillen DL (2009) Repeated hospital encounters for asthma in children and exposure to traffic-related air pollution near the home. Ann Allergy Asthma Immunol 102(2):138–144

Ebelt ST, Wilson WE, Brauer M (2005) Exposure to ambient and nonambient components of particulate matter—a comparison of health effects. Epidemiology 16(3):396–405

Fung K, Chow JC, Watson JG (2002) Evaluation of OC/EC speciation by thermal manganese dioxide oxidation and the IMPROVE method. J Air Waste Manage Assoc 52(11):1333–1341

Gauderman WJ, Avol E, Lurmann F, Kuenzli N, Gilliland F, Peters J, McConnell R (2005) Childhood asthma and exposure to traffic and nitrogen dioxide. Epidemiology 16(6):737–743

Gauderman WJ, Vora H, McConnell R, Berhane K, Gilliland F, Thomas D, Lurmann F, Avol E, Kunzli N, Jerrett M, Peters J (2007) Effect of exposure to traffic on lung development from 10 to 18 years of age: a cohort study. Lancet 369(9561):571–577

Goswami E, Larson T, Lumley T, Liu LJ (2002) Spatial characteristics of fine particulate matter: identifying representative monitoring locations in Seattle, Washington. J Air Waste Manage Assoc 52 (3):324–333

Hoek G, Beelen R, de Hoogh K, Vienneau D, Gulliver J, Fischer P, Briggs D (2008) A review of land-use regression models to assess spatial variation of outdoor air pollution. Atmos Environ 42(33):7561–7578

Jansen KL, Larson TV, Koenig JQ, Mar TF, Fieidsl C, Stewart J, Lippmann M (2005) Associations between health effects and particulate matter and black carbon in subjects with respiratory disease. Environ Health Perspect 113(12):1741–1746

Jerrett M, Arain A, Kanaroglou P, Beckerman B, Potoglou D, Sahsuvaroglu T, Morrison J, Giovis C (2005) A review and evaluation of intraurban air pollution exposure models. J Expo Anal Environ Epidemiol 15(2):185–204

Johannesson S, Gustafson P, Molnar P, Barregard L, Sallsten G (2007) Exposure to fine particles (PM2.5 and PM1) and black smoke in the general population: personal, indoor, and outdoor levels. J Expo Sci Environ Epidemiol 17(7):613–624

Kim S, Shen S, Sioutas C, Zhu YF, Hinds WC (2002) Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles basin. J Air Waste Manage Assoc 52(3):297–307

Kirchstetter TW, Corrigan CE, Novakov T (2001) Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. Atmos Environ 35(9):1663–1671

Koenig JQ, Mar TF, Allen RW, Jansen K, Lumley T, Sullivan JH, Trenga CA, Larson T, Liu LJ (2005) Pulmonary effects of indoor- and outdoor-generated particles in children with asthma. Environ Health Perspect 113(4):499–503

Krudysz MA, Froines JR, Fine PM, Sioutas C (2008) Intra-community spatial variation of size-fractionated PM mass, OC, EC, and trace elements in the Long Beach, CA area. Atmos Environ 42(21):5374–5389

Künzli N, McConnell R, Bates D, Bastain T, Hricko A, Lurmann F, Avol E, Gilliland F, Peters J (2003) Breathless in Los Angeles: the exhausting search for clean air. Am J Public Health 93(9):1494–1499

Landis MS, Norris GA, Williams RW, Weinstein JP (2001) Personal exposures to PM2.5 mass and trace elements in Baltimore, MD, USA. Atmos Environ 35(36):6511–6524

Liu LJ, Slaughter JC, Larson TV (2002) Comparison of light scattering devices and impactors for particulate measurements in indoor, outdoor, and personal environments. Environ Sci Technol 36(13):2977–2986

Liu LJ, Box M, Kalman D, Kaufman J, Koenig J, Larson T, Lumley T, Sheppard L, Wallace L (2003) Exposure assessment of particulate matter for susceptible populations in Seattle. Environ Health Perspect 111(7):909–918

Liu LJ, Curjuric I, Keidel D, Heldstab J, Kunzli N, Bayer-Oglesby L, Ackermann-Liebrich U, Schindler C (2007) Characterization of source-specific air pollution exposure for a large population-based Swiss cohort (SAPALDIA). Environ Health Perspect 115 (11):1638–1645

Long CM, Suh HH, Koutrakis P (2000) Characterization of indoor particle sources using continuous mass and size monitors. J Air Waste Manage Assoc 50(7):1236–1250

McConnell R, Berhane K, Yao L, Jerrett M, Lurmann F, Gilliland F, Kunzli N, Gauderman J, Avol E, Thomas D, Peters J (2006) Traffic, susceptibility, and childhood asthma. Environ Health Perspect 114(5):766–772

McCreanor J, Cullinan P, Nieuwenhuijsen MJ, Stewart-Evans J, Malliarou E, Jarup L, Harrington R, Svartengren M, Han IK, Ohman-Strickland P, Chung KF, Zhang J (2007) Respiratory effects of exposure to diesel traffic in persons with asthma. N Engl J Med 357(23):2348–2358

Meng QY, Turpin BJ, Korn L, Weisel CP, Morandi M, Colome S, Zhang JJ, Stock T, Spektor D, Winer A, Zhang L, Lee JH, Giovanetti R, Cui W, Kwon J, Alimokhtari S, Shendell D, Jones J, Farrar C, Maberti S (2005) Influence of ambient (outdoor) sources on residential indoor and personal PM2.5 concentrations: analyses of RIOPA data. J Expo Anal Environ Epidemiol 15(1):17–28

Meng YY, Wilhelm M, Rull RP, English P, Ritz B (2007) Traffic and outdoor air pollution levels near residences and poorly controlled asthma in adults. Ann Allergy Asthma Immunol 98(5):455–463

Molitor J, Molitor NT, Jerrett M, McConnell R, Gauderman J, Berhane K, Thomas D (2006) Bayesian modeling of air pollution health effects with missing exposure data. Am J Epidemiol 164 (1):69–76

Molitor J, Jerrett M, Chang CC, Molitor NT, Gauderman J, Berhane K, McConnell R, Lurmann F, Wu J, Winer A, Thomas D (2007) Assessing uncertainty in spatial exposure models for air pollution health effects assessment. Environ Health Perspect 115(8):1147–1153

Na KS, Sawant AA, Song C, Cocker DR (2004) Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California. Atmos Environ 38(9):1345–1355

Nethery E, Leckie SE, Teschke K, Brauer M (2008) From measures to models: an evaluation of air pollution exposure assessment for epidemiological studies of pregnant women. Occup Environ Med 65(9):579–586

Olson DA, Norris GA (2005) Sampling artifacts in measurement of elemental and organic carbon: low-volume sampling in indoor and outdoor environments. Atmos Environ 39(30):5437–5445

Pang YB, Gundel LA, Larson T, Finn D, Liu LJS, Claiborn CS (2002) Development and evaluation of a personal particulate organic and mass sampler. Environ Sci Technol 36(23):5205–5210

Pope CA 3rd, Dockery DW (2006) Health effects of fine particulate air pollution: lines that connect. J Air Waste Manage Assoc 56 (6):709–742

Ryan PH, LeMasters GK (2007) A review of land-use regression models for characterizing intraurban air pollution exposure. Inhal Toxicol 19(1 supp 1):127–133

Ryan PH, LeMasters G, Biagini J, Bernstein D, Grinshpun SA, Shukla R, Wilson K, Villareal M, Burkle J, Lockey J (2005) Is it traffic

type, volume, or distance? Wheezing in infants living near truck and bus traffic. J Allergy Clin Immunol 116(2):279–284

Ryan PH, LeMasters GK, Levin L, Burkle J, Biswas P, Hu S, Grinshpun S, Reponen T (2008) A land-use regression model for estimating microenvironmental diesel exposure given multiple addresses from birth through childhood. Sci Total Environ 404 (1):139–147

Sarnat JA, Holguin F (2007) Asthma and air quality. Curr Opin Pulm Med 13(1):63–66

Strand M, Vedal S, Rodes C, Dutton SJ, Gelfand EW, Rabinovitch N (2006) Estimating effects of ambient PM(2.5) exposure on health using PM(2.5) component measurements and regression calibration. J Expo Sci Environ Epidemiol 16(1):30–38

Trasande L, Thurston GD (2005) The role of air pollution in asthma and other pediatric morbidities. J Allergy Clin Immunol 115 (4):689–699

Trenga CA, Sullivan JH, Schildcrout JS, Shepherd KP, Shapiro GG, Liu LJS, Kaufman JD, Koenig JQ (2006) Effect of particulate air pollution on lung function in adult and pediatric subjects in a Seattle panel study. Chest 129(6):1614–1622

Turpin BJ, Huntzicker JJ, Hering SV (1994) Investigation of organic aerosol sampling artifacts in the Los Angeles basin. Atmos Environ 28(19):3061–3071

Turpin BJ, Saxena P, Andrews E (2000) Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos Environ 34(18):2983–3013

Van Roosbroeck S, Wichmann J, Janssen NA, Hoek G, van Wijnen JH, Lebret E, Brunekreef B (2006) Long-term personal exposure to traffic-related air pollution among school children, a validation study. Sci Total Environ 368(2–3):565–573

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

Van Roosbroeck S, Hoek G, Meliefste K, Janssen NAH, Brunekreef B (2008) Validity of residential traffic intensity as an estimate of long-term personal exposure to traffic-related air pollution among adults. Environ Sci Technol 42(4):1337–1344

Wu CF, Delfino RJ, Floro JN, Samimi BS, Quintana PJ, Kleinman MT, Liu LJ (2005a) Evaluation and quality control of personal nephelometers in indoor, outdoor and personal environments. J Expo Anal Environ Epidemiol 15(1):99–110

Wu J, Funk TH, Lurmann FW, Winer AM (2005b) Improving spatial accuracy of roadway networks and geocoded addresses. Trans GIS 9:585–601

Wu J, Lurmann F, Winer A, Lu R, Turco R, Funk T (2005c) Development of an individual exposure model for application to the Southern California children's health study. Atmos Environ 39(2):259–273

Wu J, Houston D, Lurmann F, Ong P, Winer A (2009) Exposure of PM2.5 and EC from diesel and gasoline vehicles in communities near the Ports of Los Angeles and Long Beach, California. Atmos Environ 43(12):1962–1971

Zhu YF, Hinds WC, Kim S, Shen S, Sioutas C (2002) Study of ultrafine particles near a major highway with heavy-duty diesel traffic. Atmos Environ 36(27):4323–4335

Article 2: Role of highway traffic on spatial and temporal distributions of air pollutants in a Swiss Alpine valley

Regina E. Ducret-Stich[1,2], Ming-Yi Tsai[1,2,3], Martina S. Ragettli[1,2], Alex Ineichen[1,2], Nino Kuenzli[1,2], Harish C. Phuleria[1,2]

[1] Department of Epidemiology and Public Health, Swiss Tropical and Public Health Institute, Socinstrasse 57, 4002 Basel, Switzerland

[2] University of Basel, 4003 Basel, Switzerland

[3] Department of Environmental & Occupational Health Sciences, University of Washington, Seattle, WA 98195 USA

This article has been published in the journal Science of the Total Environment

Science of the Total Environment 456–457 (2013) 50–60

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Role of highway traffic on spatial and temporal distributions of air pollutants in a Swiss Alpine valley

Regina E. Ducret-Stich [a,b,*], Ming-Yi Tsai [a,b,c], Martina S. Ragettli [a,b], Alex Ineichen [a,b], Nino Kuenzli [a,b], Harish C. Phuleria [a,b]

[a] Department of Epidemiology and Public Health, Swiss Tropical and Public Health Institute, Socinstrasse 57, 4002 Basel, Switzerland
[b] University of Basel, 4003 Basel, Switzerland
[c] Department of Environmental & Occupational Health Sciences, University of Washington, Seattle, WA 98195, USA

HIGHLIGHTS

- One of the first studies characterizing air pollution exposures in an Alpine valley
- Traffic-related air pollutant concentrations decay within 200 m from the highway.
- Daily trends of NO2, PM10, EC and PN follow the heavy-duty traffic counts.
- Hybrid model successfully estimates daily residential outdoor NO2 in the community.

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form 20 February 2013
Accepted 17 March 2013
Available online 11 April 2013

Keywords:
Air pollution exposure
Highway traffic
Modeling
Alpine valley
Nitrogen dioxide

ABSTRACT

Traffic-related air pollutants show high spatial variability near roads, posing a challenge to adequately assess exposures. Recent modeling approaches (e.g. dispersion models, land-use regression (LUR) models) have addressed this but mostly in urban areas where traffic is abundant. In contrast, our study area was located in a rural Swiss Alpine valley crossed by the main North–south transit highway of Switzerland.

We conducted an extensive measurement campaign collecting continuous nitrogen dioxide (NO_2), particulate number concentrations (PN), daily respirable particulate matter (PM_{10}), elemental carbon (EC) and organic carbon (OC) at one background, one highway and seven mobile stations from November 2007 to June 2009. Using these measurements, we built a hybrid model to predict daily outdoor NO_2 concentrations at residences of children participating in an asthma panel study.

With the exception of OC, daily variations of the pollutants followed the temporal trends of heavy-duty traffic counts on the highway. In contrast, variations of weekly/seasonal means were strongly determined by meteorological conditions, e.g., winter inversion episodes. For pollutants related to primary exhaust emissions (i.e. NO_2, EC and PN) local spatial variation strongly depended on proximity to the highway. Pollutant concentrations decayed to background levels within 150 to 200 m from the highway.

Two separate daily NO_2 prediction models were built using LUR approaches with (a) short-term traffic and weather data (model 1) and (b) subsequent addition of daily background NO_2 to previous model (model 2). Models 1 and 2 explained 70% and 91% of the variability in outdoor NO_2 concentrations, respectively. The biweekly averaged predictions from the final model 2 agreed very well with the independent biweekly integrated passive measurements taken at thirteen homes and nine community sites (validation $R^2 = 0.74$). The excellent spatio-temporal performance of our model provides a very promising basis for the health effect assessment of the panel study.

1. Introduction

In the last decade, epidemiologic studies have shown evidence of ambient air pollution as a major risk factor for various diseases, especially cardio-respiratory diseases (Kelly and Fussell, 2011; Kuenzli et al., 2010). Children are particularly susceptible to the effects of air pollution exposure as their lungs are still in development (Gauderman et al., 2007). Of particular interest and policy relevance are source specific health effects with traffic related air pollution being emphasized in many studies due to the constant increase in traffic and the proximity of this combustion source to people's homes and work places (HEI, 2010). Due to health concerns raised

* Corresponding author at: Swiss TPH, Socinstrasse 57, P.O. Box 4002 Basel, Switzerland. Tel.: +41 61 284 86 16; fax: +41 61 284 81 01.
E-mail address: regina.ducret@unibas.ch (R.E. Ducret-Stich).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.03.065

in communities along the main North–south transit route crossing the Alps in Switzerland (Hazenkamp-von Arx et al., 2011), federal authorities in charge of monitoring the impact of the transit traffic funded this panel study to investigate the short-term effects of local traffic-related air pollution on the course of asthma in children.

Central fixed site measurements are often used to describe the air pollution exposure for a specific region in epidemiological studies. However, these measurements cannot adequately represent local traffic-related air pollution which shows high small scale spatial variability (Goswami et al., 2002; Liu et al., 2007; Padró-Martínez et al., 2012; Zhu et al., 2002). Alternatively, air pollution models such as dispersion or land-use regression (LUR) models are used (Hoek et al., 2008; Jerrett et al., 2004). Because of the coarse resolution of dispersion models they are not adequate for small-scale local situations and are not reliable for areas with special topographic conditions like in Swiss Alpine valleys (Liu et al., 2007). LUR models on the other hand perform better for small areas and are able to describe also small-scale variations by integrating local topographical and meteorological data. The latter is particularly important in our case as the topography in this Alpine region influences wind systems and the formation of inversion layers in winter and therefore has a great impact on the air pollution distribution in the valley. Similar topographic situations were described for the region of the Inn valley in Austria (Gohm et al., 2009; Harnisch et al., 2008; Schäfer et al., 2008; Schnitzhofer et al., 2009) or the Brenner Pass in Italy (de Franceschi and Zardi, 2008).

However, LUR models are mostly used for long-term exposure assessments (Hoek et al., 2008), whereas so called “hybrid models” (Jerrett et al., 2004) are able to provide spatially resolved short-term (mostly biweekly) exposure estimates by combining LUR models with short-term temporal data such as meteorological variables (Ainslie et al., 2008; Arain et al., 2007; Liu et al., 2012; Mavko et al., 2008; Su et al., 2008) or fixed site monitoring measurements (Rose et al., 2010). We went one step further and combined the LUR model with both, meteorological and fixed site air pollution data for modeling daily NO_2. A similar approach was used by Maynard et al. (2007) for black carbon.

This publication has thus two objectives. First, we describe the air quality in the study area with a particular emphasis on the local traffic-related pollution, its temporal patterns, and its dependence on highway A2 using both primary and secondary markers of air pollution. Second, we develop models to estimate daily concentrations of ambient NO_2 at any site for later use in the asthma panel study. We combine land-use regression approaches with short-term data on traffic, weather and pollution and validate our model with a large number of independent biweekly aggregated NO_2 measurements. These modeled exposure estimates will ultimately be used for assessing acute health effects.

2. Methods

2.1. Study area

This work is part of an asthma panel study evaluating short-term effects of highway traffic air pollution on respiratory health in 13 children living in Erstfeld, a village with about 3800 habitants located in a rather narrow and flat Alpine valley of some 800–900 m width bordered by steep mountain slopes on both sides in Switzerland. Running along this valley is the highway A2 which is the major transit route between Northern and Southern Europe crossing the Alps through the Gotthard tunnel. In 2008, nearly 975,000 heavy duty vehicles passed this tunnel, accounting for 76% of the total Swiss heavy duty transit traffic (Federal Office of Transport, 2011). This traffic load contributes greatly to the air pollution in the villages in this valley.

2.2. Study design

From November 2007 to June 2009, several air pollutants were measured continuously at a fixed background, a fixed highway and seven different locations in the valley through a rotating mobile station. The highway and background sites measured throughout this duration while the mobile station measured for a month each time before switching to the next site. In addition, passive samplers were deployed at the same stations, at nine additional community outdoor sites scattered throughout the village and inside and outside of 13 children's homes to measure integrated biweekly NO_2 levels (Fig. 1). The various pollutants and measuring frequency for the different sites are described in Table 1. At the highway, background and mobile site temperature, wind speed and direction, and relative humidity (only at highway site) were also collected. Hourly traffic counts on the highway and the main street were obtained from the Federal roads office FEDRO (Federal administration, Bern, Switzerland).

2.2.1. Measurement site description

The background site was situated outside the residential area 429 m away from the highway and 280 m from the main road in an open field. The highway site, located north of the village right beside the highway (22 m from centerline), is one of the six continuous measuring sites used to monitor air pollution levels along the A2 highway by the Federal Office of the Environment in Switzerland

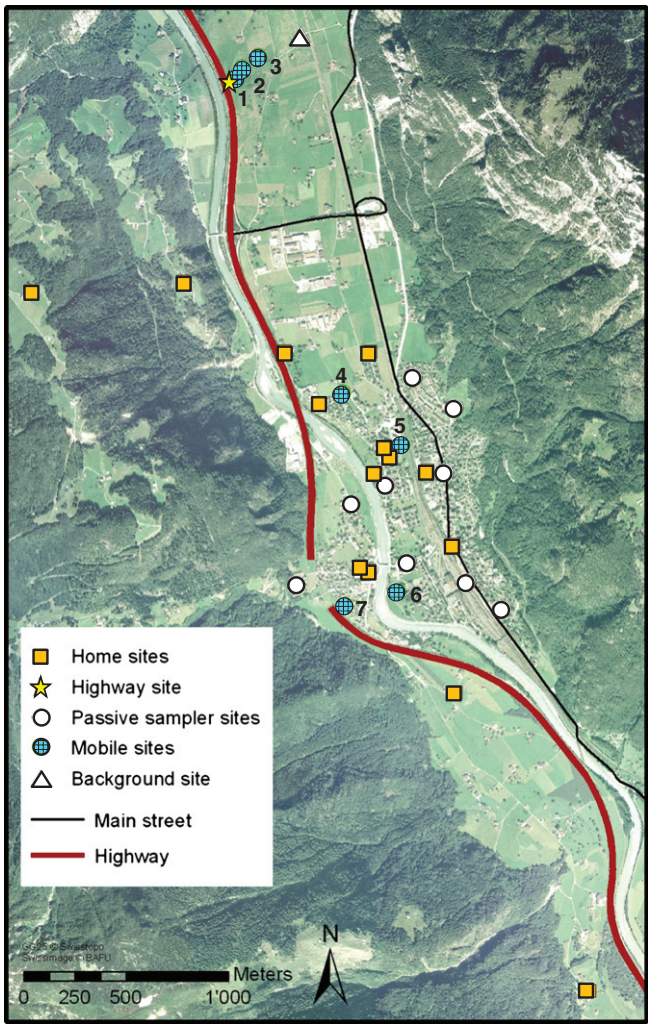


Fig. 1. Map of Erstfeld with home locations and measurement sites.

Table 1
Type and frequency of measured pollutants at different sites.

Sites	Distance to center line of highway (m)	Monitoring time	Pollutant	Type of measurement
Highway	22	Nov 2007–June 2009	NO, NO_2, NO_x, PN, O_3	Continuous
			PM_{10}, EC, OC	24-Hour
			NO_2	14-Days (passive)
Background	429	Nov 2007–June 2009	NO, NO_2, NO_x, PN	Continuous
			NO_2	14-Days (passive)
7 mobile sites	49, 55, 102, 198, 222, 255, 450	Nov 2007–June 2009; 4 weeks per season each[a]	NO, NO_2, NO_x, PN	Continuous
			PM_{10}, EC, OC, chemical elements	24-Hour
			NO_2	14-Days (passive)
9 community outdoor sites	140–734	Nov 2007–June 2009	NO_2	14-Days (passive)
13 homes (inside and outside)	27–979	14 days before each health measurement	NO_2	14-Days (passive)

[a] The mobile station was rotated each month to another site in order to optimize the data collection and ensure measurements in each of the four seasons at all of the sites.

(project: Monitoring of Supporting Measures — Environment) since 2003. Three of the mobile sites were located between the highway and the background site perpendicular to the highway at a distance of 55, 102 and 198 m (Fig. 1 (sites 1–3), Table 1). The other four mobile sites were situated within the residential area (Fig. 1 (sites 4–7), Table 1). They were chosen to represent different distances from the highway, the main road and train tracks and different regions from North to South. The northern region was represented by site 4, which was located in the middle between the highway and the main road/train track (222 m and 261 m/251 m, respectively), and by site 5, which was very close to the train tracks (22 m) and away from the highway and main road (450 m and 147 m, respectively). The southern part of the residential area was represented by sites 6 and 7. Site 6, was close to the school of the participating children and located between highway and main road/train track (255 m and 335 m/262 m, respectively). Site 7 was close to the highway (49 m) right next to the end of a tunnel (in no-tunnel area) at a location where the highway was lined with a noise barrier (Fig. 1, site 7). Thus this site was partly protected from highway-related air pollutants by both the noise barrier and the tunnel.

2.3. Air pollution measurements

2.3.1. Continuous measurements

All measurements at the highway, mobile and background sites were collected and controlled for quality by inNET Monitoring AG (Altdorf, Switzerland). Continuous measurements were reported as 30-min values and consisted of nitrogen oxides (NO and NO_2) monitored by chemiluminescence (ML 9841, Monitor Labs), particle number concentration (PN) measured with a condensation particle counter (CPC 3022A, TSI Inc., Shoreview, MN) and ozone (O_3) quantified with ultraviolet absorption method (ML 9810, Monitor Labs). Particulate matter with an aerodynamic diameter <10 μm (PM_{10}) was collected for every 24 h on pre-conditioned (48 h at 22 °C and 50% RH) pre-weighted 150 mm quartz fiber filters (Pallflex Tissuquartz 2500QAT-UP, Pall AG, Switzerland) using High Volume Samplers (Digitel DHA-80) with a flow rate of 500 L/min. Mass concentration was subsequently determined by standard gravimetric methods. The limit of detection (LOD), defined as three times the standard deviation of the field blanks ($N = 64$), was 3.0 μg/m^3. All filters were analyzed for elemental (EC) and organic carbon (OC) with thermal–optical transmission method (TOT, OCEC Analyzer Sunset Laboratory Inc.). Due to a protocol change starting Jan 2009 at the analysis facility (Carbotech AG, Basel, Switzerland) all filters collected in 2009 were analyzed with a different temperature profile. Filters from 2007 to 2008 were analyzed with the NIOSH700$^+$ protocol which is a variation of the He4-700 protocol described in Subramanian et al. (2006). It consists of the helium phases He1 at 310 °C (70 s), He2 at 475 °C (60 s), He3 at 615 °C (60 s) and He4 at 700 °C (180 s) and the oxidation phases HeOx1 at 550 °C (45 s), HeOx2 at 625 °C (45 s), HeOx3 at 700 °C (45 s), HeOx4 at 775 °C (45 s) and HeOx5 at 870 °C (90 s). Filters from the year 2009 were analyzed with the EUSAAR2 protocol (Cavalli et al., 2010). To utilize all the data in the analysis we adjusted NIOSH derived EC and OC to EUSAAR2 derived EC and OC by multiplying the NIOSH data with the factor 1.1 and 0.92 for EC and OC, respectively. These factors were obtained from orthogonal regression analysis of 102 ambient filters collected at five sites from the national air pollution monitoring network (NABEL) with varying concentrations (from rural background to traffic affected urban) which were analyzed with both protocols (personal communication with Fischer Andrea, EMPA, Dübendorf, Switzerland).

2.3.2. Integrated passive NO_2 measurements

Biweekly integrated NO_2 levels were measured with passive diffusion samplers (Passam AG, Männedorf, Switzerland), at the highway, the background, seven mobile and nine additional sites in the village throughout the study period (each tube measuring two weeks every time). Additionally, the parents of the above recruited children were instructed to deploy passive samplers both indoors and outdoors during the 14-day periods prior to each of the repeated health measurements organized as part of the panel study. The tubes were protected with a rain cover and placed either outside the sleeping room window of the child, on the balcony or in the garden.

2.4. Meteorological parameters

Temperature and relative humidity were measured 2 m above ground with a thermo hygrometer (WNZ, Meteolabor AG, Wetzikon, Switzerland). A wind gauge measured wind speed and direction in 10 m height above ground (WNZ, Meteolabor AG, Wetzikon, Switzerland). All measurements were reported as 30-min values. Average daily wind speed and direction were determined by wind vectors calculated as the vector sum of the 30-min wind speeds and directions over a day.

We observed a distinct mountain wind system in this valley with diurnally changing wind directions, southerly in the night and morning, and northerly during the day. To account for these wind direction changes and their resulting influence on air pollution transport we calculated a downwind frequency for each site defined as the number of hours per day the wind blew from the highway to the monitoring site. We also calculated a stagnation index, defined as the number of hours per day when the wind speed was below the overall median wind speed (Norris et al., 2000), to account for the days with potential inversion or a stable atmosphere with very low degree of dispersion.

2.5. Traffic counts

Hourly traffic counts on the highway and the main road were obtained from the Federal roads office FEDRO (Federal administration Bern, Switzerland) for seven vehicle categories. These were combined

to two new categories: heavy-duty vehicles (HDV) including trucks with semi-trailers, trucks with trailers, trucks and buses, and light-duty vehicles (LDV) including cars, vans and motor bikes. Hourly counts were summed up to daily counts for all the analysis. The traffic counts on the main road were only available for part of the study period (Jul 2008 to Jun 2009), hence we imputed the traffic counts for the missing period (Nov 2007 to Jun 2008) using the measured data from Jul 2008 to Jun 2009 and matching them by weekdays and holidays assuming the traffic volume and pattern did not change much from 2007 to 2009.

2.6. Statistical analysis

Daily averages were derived from the continuous measurements. Since the measurements at the seven mobile sites spanned across different months, we combined them to one time series in order to compare long-term averages. Summary statistics and Spearman correlations were thus calculated for the highway, mobile and background sites.

Given the spatial contrast in traffic related pollutants such as NO_2 amid the highway, background and the seven mobile sites, first, a multivariate linear regression model (model 1) was built using available geographical parameters – describing the spatial variation – as well as temporally resolved variables such as traffic counts, meteorological and temporal/seasonal parameters. Traffic counts were weighted by the inverse log-distance to account for the rather logarithmic decay of traffic-related air pollution concentrations away from the source (Goswami et al., 2002; Padró-Martínez et al., 2012; Zhu et al., 2002). Second, we included additional variables for background pollutant levels to model 1 (model 2) to further refine the temporal variation of the model. All tested predictors are summarized in Table 4.

Backward and forward stepwise selection procedures, with a 0.1 significance level chosen for a covariate entering or staying in the model, were used to select the final models. After exclusion of models with physically unrealistic estimates, i.e. opposite direction of effects, both procedures resulted in the same final models. The models were validated by 10-fold cross-validation approach (Hastie et al., 2001). The measurements were randomly divided into ten groups with one group (10% of data, test data) retained for model testing, while the rest (90% of data, training data) was used for model fitting. The procedure was repeated for all ten groups. Adjusted R^2s, root mean squared errors (RMSE) and differences between the predictions and measurements (bias) are reported. In addition we validated our final model against independent measurements by comparing the matched biweekly averaged predictions with the passive measurements at the home and community outdoor sites. As half of the data used to fit the models were from the highway site, we performed a sensitivity analysis by excluding the highway data in the training set. All statistical analyses were performed with SAS 9.2 (SAS Institute Inc., Cary, NC, USA).

3. Results and discussion

3.1. Air pollution distribution

3.1.1. Annually averaged concentrations

Table 2 presents a summary of the measured air pollutants and meteorological parameters at the highway, background and combined mobile sites as well as traffic counts on the highway and main road. Results are presented for the year 2008 instead of the whole study period to avoid over-representing the winter months. With the exception of PM_{10} and OC, the highway site observed the highest annual concentrations of all the pollutants. Concentrations at the mobile sites were similar to those at the background site. Annually averaged PM_{10} and OC were not different between highway and mobile sites. Mean annual NO_2 levels at the highway exceeded the Swiss annual air quality standard of 30 μg/m^3. While annual PM_{10} levels at the highway and mobile sites stayed below the limit of 20 μg/m^3, the daily limit of 50 μg/m^3, not to be exceeded more than once per year, was violated three times in 2008. A comparison with other Swiss monitoring sites from the NABEL (National Air Pollution Monitoring Network) network showed similar concentrations for traffic related pollutants (NO_2, EC and PN) at the highway site in Erstfeld and the urban site in Lugano, while the mobile and background concentrations in Erstfeld were more comparable to the suburban site in Basel—Binningen (BAFU, 2009). PM_{10} concentrations, which were similar at the highway and mobile sites, were comparable with levels at suburban (Basel—Binningen, Dübendorf) and rural (Payerne, Tänikon) NABEL sites as well as other rural background sites in Europe (Putaud et al., 2010). Mean daily ozone (O_3) concentrations at the highway in Erstfeld were comparable to levels at NABEL traffic sites (BAFU, 2009).

Table 2
Grand summary statistics of measured parameters for the year 2008.

	Site	N	Mean	SD[a]	Min	Max
Air pollutants						
NO_2 (μg/m^3)[b]	Highway	366	32.3	12.2	3.2	68.1
	Mobile[c]	353	23.1	11.2	2.3	61.1
	Background	365	21.5	11.0	2.9	54.1
NO_2 (μg/m^3)[d]	Highway	26	34.2	6.5	24.3	52.5
	Mobile[c]	104	22.8	6.5	12.8	41.0
	Background	26	22.7	7.3	12.0	41.2
NO_x (μg/m^3)	Highway	366	64.0	37.5	4.3	228.6
	Mobile[c]	353	35.8	25.9	2.9	183.4
	Background	365	32.7	24.6	4.2	151.4
PM_{10} (μg/m^3)	Highway	361	16.9	10.1	1.0	93.5
	Mobile[c]	333	15.5	10.4	0.3	93.8
EC (μg/m^3)	Highway	365	1.65	0.81	0.12	4.89
	Mobile[c]	352	1.16	0.70	0.04	4.38
OC (μg/m^3)	Highway	365	2.76	1.54	0.19	9.01
	Mobile[c]	352	2.68	1.50	0.09	8.66
PN (#/cm^3)	Highway	338	17,349	7591	1034	44,538
	Mobile[c]	318	9784	4870	1480	33,166
	Background	334	8218	4062	695	25,290
O_3 (μg/m^3)[b]	Highway	365	38.4	24.0	1.7	120.1
Traffic counts						
Heavy duty vehicles (#/day)	Highway	366	3030	1451	118	5069
	Main road	366	143	35	75	234
Light duty vehicles (#/day)	Highway	366	19,010	8040	7812	47,995
	Main road	366	7047	1311	2876	10,434
Meteorological data						
Wind speed (m/s)	Highway	363	1.41	2.05	0.03	15.39
	Mobile[c]	329	0.99	1.28	0.01	9.23
	Background	229	1.50	2.00	0.04	13.43
Temperature (°C)	Highway	359	10.9	6.9	−2.6	24.7
	Mobile[c]	346	9.7	6.8	−3.4	24.0
	Background	365	10.4	7.0	−3.2	24.5
Relative humidity (%)	Highway	357	72.6	11.9	29.2	91.8

[a] Standard deviation.
[b] Based on daily averages of the continuous monitor data.
[c] Single time series containing measurements from all seven mobile sites.
[d] Based on biweekly integrated passive sampler data.

3.1.2. Correlations

Spearman correlations, ρ, of the daily pollution measurements, calculated for each site, are listed in Table 3. Correlations at the highway site were high between NO_2, EC and PN (ρ = 0.72–0.83) and also between PM_{10} and OC (ρ = 0.84); whereas, correlations of pollutants between the two groups were moderate (ρ = 0.35–0.61) (Table 3). However, at the mobile sites only low to moderate correlations were observed between all the pollutants (Table 3). These lower correlations at the mobile sites might be partly due to the distance to the highway. Earlier studies reported high correlations for traffic-related pollutants (such as PN, NO, NO_x, black carbon, polycyclic aromatic hydrocarbons (PAHs)) measured directly on highways (Westerdahl et al., 2005; Fruin et al., 2008) while Padró-Martínez et al. (2012) showed similar

Table 3
Spearman correlations ρ (N) among different pollutants by site for the year 2008.

		NO_2	PM_{10}	EC	OC
Highway	PM_{10}	0.51** (361)			
	EC	0.73** (365)	0.61** (360)		
	OC	0.60** (365)	0.84** (360)	0.80** (365)	
	PN	0.83** (338)	0.35** (333)	0.72** (337)	0.50** (337)
Mobile (7 sites)	PM_{10}	0.04 to 0.63** (27 to 82)			
	EC	−0.61 to 0.35* (27 to 82)	−0.12 to 0.28* (27 to 82)		
	OC	−0.61 to 0.20* (27 to 82)	−0.24 to 0.37* (27 to 82)	0.59** to 0.93** (27 to 82)	
	PN	−0.14 to 0.56** (27 to 82)	−0.03 to 0.60** (27 to 82)	−0.26 to 0.52** (27 to 82)	−0.53 to 0.32* (27 to 82)
Background	PN	0.82** (334)			

** $p < 0.01$.
* $p < 0.05$.

correlations to our mobile sites for measurements done within 400 m of a highway. Additionally, the uneven and substantially low number of measurements among the mobile sites might have influenced the correlations. Some mobile sites were well represented by different seasons resulting in moderate correlations while others were dominated by a single season hence low correlation.

3.1.3. Temporal and seasonal variation

As shown in Fig. 2 light vehicle traffic counts were clearly higher on the weekends, whereas heavy-duty traffic decreased with values approaching zero on Sunday when trucks are not allowed to drive. The weekday pattern of all pollutants and at all sites followed the heavy-duty traffic patterns with lowest concentrations measured on Sundays. This was particularly obvious for NO_2, EC and particle numbers (peaks on Thursday), all originating from exhaust emissions. The weekend trends were rather marginal in the case of OC and PM_{10} where Sunday means were only 12% and 16% below the weekday levels, respectively. In contrast PM_{10} showed a quite distinct peak on Wednesday. Non-exhaust roadway emissions (break and tire wear, road wear) and resuspended road dust constitute a significant part of the PM_{10} (Gehrig et al., 2004) and result from not only heavier vehicles but passenger cars too. The relative contribution of passenger cars is, however, lower (Gehrig et al., 2004), which is also consistent with the fact that near the highway site there is a relative decrease in PM_{10} on Sunday (lowest truck traffic) that is significantly lower (16%) than in other pollutants (25 to 30% for NO_2, EC, PN). Similar weekday trends were observed in a mobile monitoring study done near a highway in Somerville, Massachusetts for PN, NO_x, NO, black carbon, $PM_{2.5}$, CO and PAHs (Padró-Martínez et al., 2012).

The above described traffic impact on pollutants disappeared when changing the temporal resolution from daily to weekly averages. While heavy-duty vehicle traffic stayed more or less constant over the year and light vehicle traffic increased in summer, no such trend could be observed in air pollution levels (Fig. 3). Quite the contrary was shown by NO_2 with generally lower concentrations in summer paired with high weekly variation reflecting changing meteorological conditions (Fig. 3a). The same weekly trends were observed for EC and particle number concentrations (results not shown). PM_{10} (Fig. 3b) and OC (results not shown) showed high weekly variability with less pronounced seasonal trends. Higher air pollution levels in winter (Fig. 4) were expected as less pronounced mountain winds and frequent inversion episodes likely lead to an accumulation of air pollution in the valley (Gohm et al., 2009). These conditions, in fact, are also responsible for the more homogeneous spatial distribution observed in our measurements in winter compared to summer.

3.1.4. Spatial variation

Traffic associated pollutants NO_2, EC and PN showed a distinct spatial pattern with highest levels near the highway and decreasing concentrations at the mobile and background sites (Table 2, Figs. 2, 3, 4). For instance, NO_2 levels dropped with increasing distance to

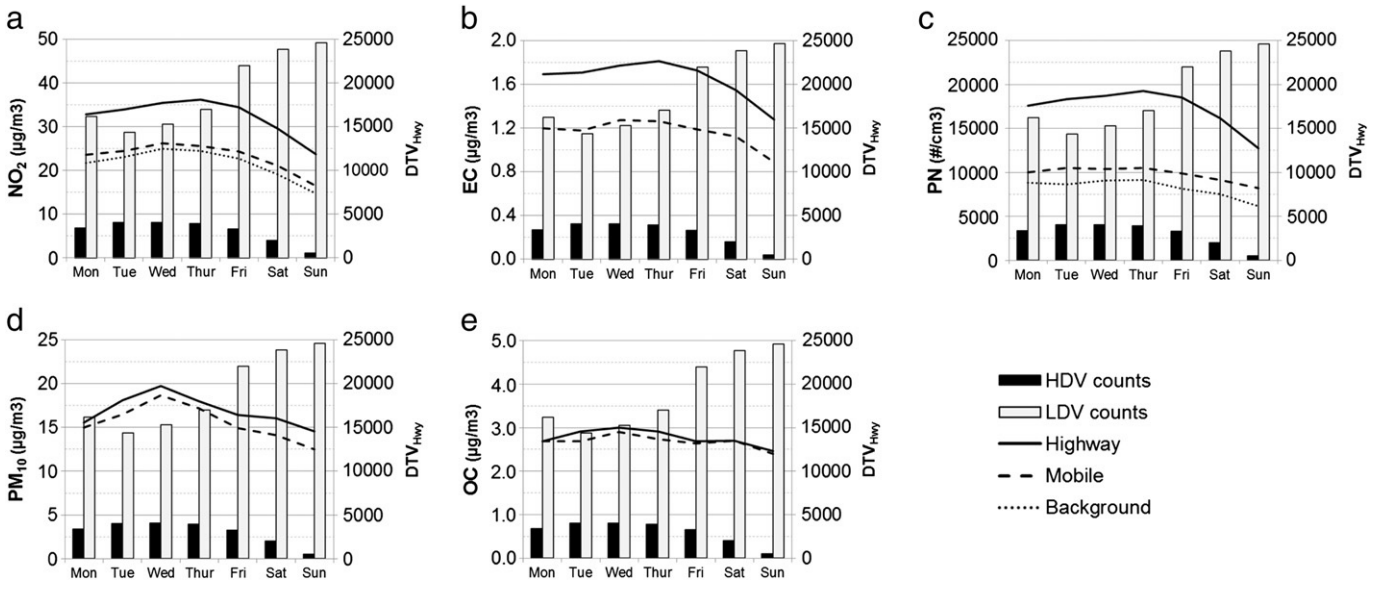


Fig. 2. Average concentrations of a) NO_2, b) EC, c) PN, d) PM_{10} and e) OC at different sites with averaged daily heavy-duty (HDV) and light-duty (LDV) traffic counts on the highway (DTV_{Hwy}) by weekday in 2008.

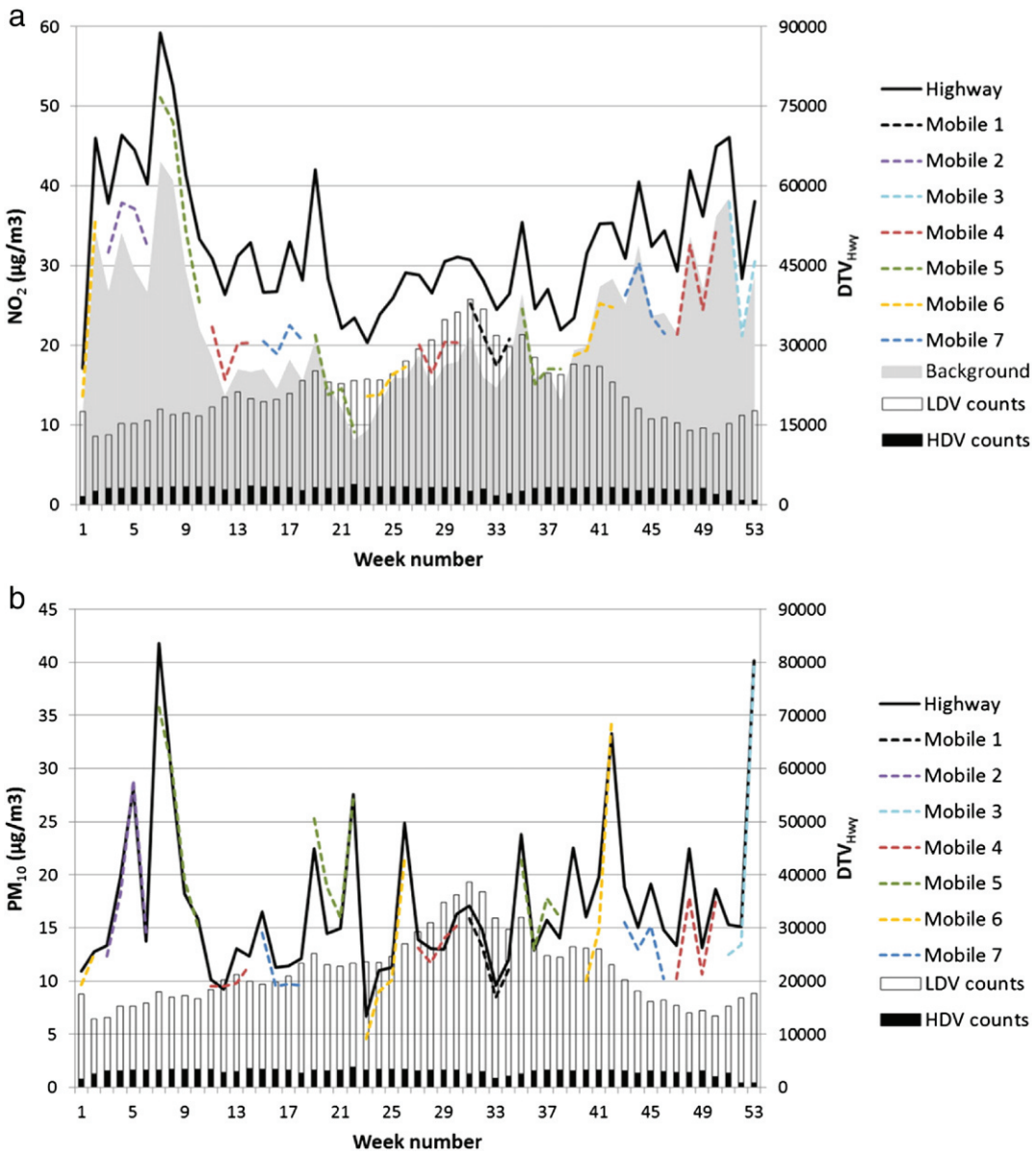


Fig. 3. Weekly averaged concentration of a) NO_2 and b) PM_{10} at different sites along with averaged daily heavy-duty vehicle (HDV) and light-duty vehicle (LDV) counts on the highway (DTV_{Hwy}) in 2008.

the highway to background levels after 150 to 200 m (Fig. 5) confirming findings from other studies (Goswami et al., 2002; Liu et al., 2007; Padró-Martínez et al., 2012; Zhu et al., 2002). This spatial decay of traffic associated pollutants away from the highway was expected as 75% of the total traffic in the valley and even 95% of the heavy-duty vehicles run on the highway. Three sites were excluded in Fig. 5 due to unexpectedly low NO_2 levels. One was the mobile site 7, which was partly protected from highway-originating air pollutants by both the noise barrier lining the highway and the adjacent tunnel, leading to lower observed pollution levels than would be expected regarding the distance to the highway. The other two were children's homes located about 120 and 580 m above the valley, where NO_2 levels were very low. There were also two outliers in Fig. 5 with a lower and a higher ratio than the surrounding sites at the homes 233 and 268 m away from highway, respectively. The first home was about 30 m above the highway and sheltered by a forest probably leading to lower concentrations than observed at the background site. For the second home only measurements from January to June 2008 ($N = 6$) were available. During this time, NO_2 was always lower at background compared to mobile sites, whereas there was mostly no difference in the second half of the year (Fig. 3a). Limiting measurements to the first half year in 2008 would therefore lead to higher ratios, as observed for the second home (Fig. 5). In contrast to traffic-related pollutants, PM_{10} and OC (influenced by additional sources) were more homogeneously distributed with similar concentrations at all sites (Table 2, Figs. 2, 3b, 4).

3.2. Modeling daily NO_2

The traffic related pollutants NO_2, EC and PN were highly correlated close to the highway (Table 3) and demonstrated high spatial (higher levels close to highway) and temporal variability at the continuous monitoring sites in the valley (Figs. 2–5). On the contrary, PM_{10} and OC showed lower spatial contrast (similar concentrations at highway, mobile and background sites) and were also (together with EC) not measured at the background site. Moreover, for NO_2, a large number of biweekly integrated NO_2 measurements were available at the children's homes and community outdoor sites, which could be used for independent validation of the models. Therefore, we chose NO_2 as a marker to model daily exposure to highway traffic in the valley.

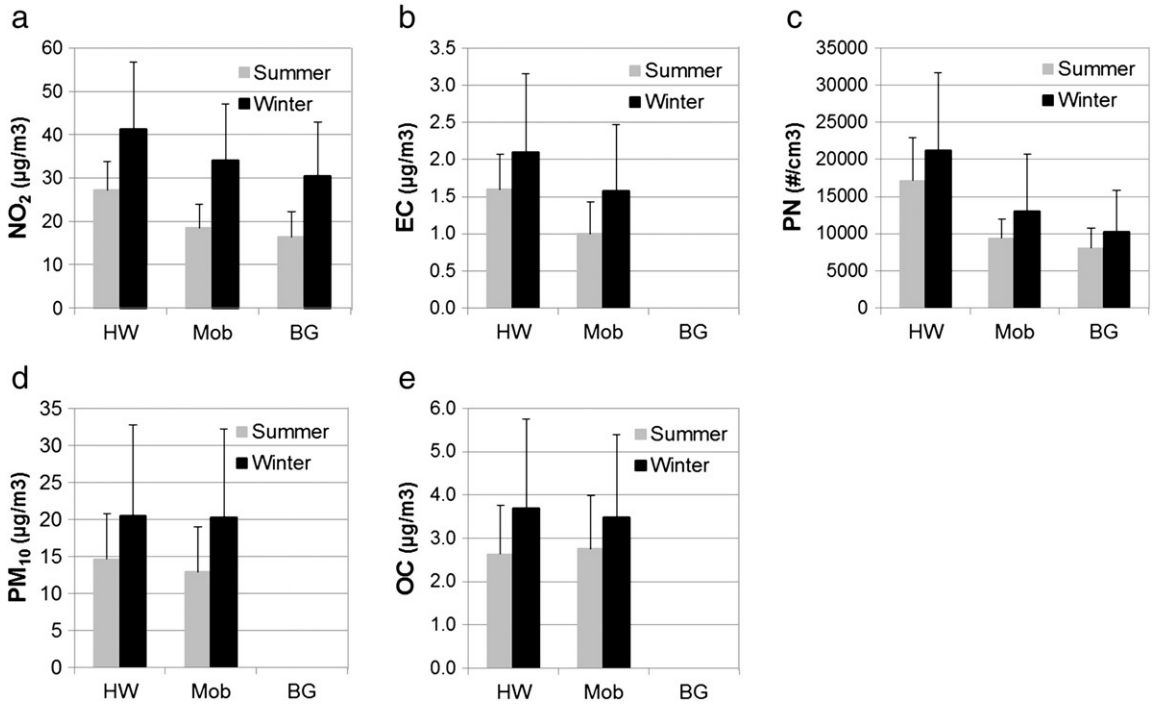


Fig. 4. Average concentrations of measured a) NO_2, b) EC, c) PN, d) PM_{10} and e) OC at the highway (HW), combined mobile (Mob) and background (BG) sites in summer (June–August) and winter (December–February) in the year 2008. Whiskers represent standard deviation.

Model 1, which included spatial and temporal predictors without using background air pollution concentrations, explained 70% (adjusted R^2) of the daily NO_2 variation as measured by the highway and the 7 mobile stations (Table 5a). The most important predictors were stagnation index, temperature, and distance weighted heavy-duty traffic counts (partial $R^2 = 0.25, 0.20, 0.19$, respectively). The addition of the daily background NO_2 into the previous model resulted in improved performance of the new model (model 2) and explained an additional 21% of the variability in outdoor NO_2 concentrations (Table 5a). While in model 1 meteorological parameters explained most of the temporal variation, they had only a minor influence in model 2 as their effects were largely reflected in the background NO_2 concentrations, which was the most important predictor (partial $R^2 = 0.76$) in model 2 (Table 5a). However, it needs to be emphasized that the background NO_2 levels were also impacted by the highway traffic. This can be corroborated by the model 1 findings where background NO_2 was not included (Table 5a): of the total 70% explained variance in model 1, >20% was explained by inverse log-distance weighted highway traffic counts only. However, in model 2, weighted traffic counts on the highway for heavy- and light-duty vehicles contributed only 6% and 7% to the explained variance, respectively (Table 5a). In model 2, heavy-duty vehicles on the highway contributed equally to NO_2 concentrations as light-duty vehicles although they only accounted for 14% of the total highway traffic, i.e. one truck contributed over eight times more to NO_2 than one car which has been shown in many laboratory and on-road emission characterization studies (EEA, 2009; Oliveira et al., 2011).

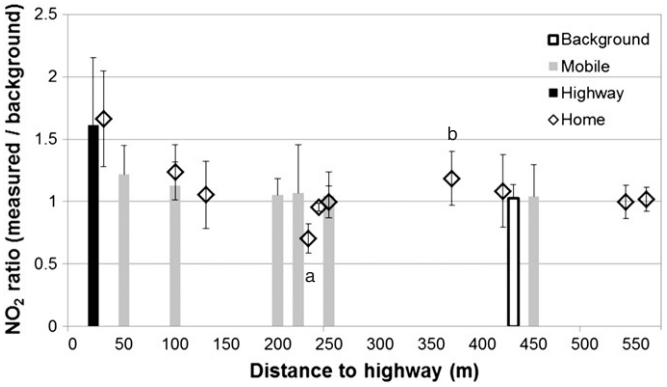


Fig. 5. Average ratio of measured biweekly NO_2 (passive sampler measurements) to the matched background NO_2 (continuous measurements) at different sites by distance to the highway for the whole study period (Nov. 2007–June 2009). Two houses at higher elevations (120 m and 580 m above valley floor) and mobile site 7 (3.1.3) were excluded. Whiskers represent standard deviation. [a]Forest between the house and highway. [b]From only 6 measurements (Jan–Jun 2008).

With an adjusted R^2 of 0.70, our daily model, without using the background measurements (model 1, Table 5a), was comparable to several annual NO_2 LUR-models (Hoek et al., 2008). Additionally, the types of variables included were also similar. The main road related variables did not enter in our model probably because it had only 25% of the total traffic and 5% of the total heavy duty traffic. Forcing the main road traffic count variables into the model did not change the model coefficients of other predictors either.

With an R^2 of 0.70 performance of our model 1 was similar to other studies, where wind variables were included in the model. In Toronto, Arain et al. (2007) reported an improvement of R^2 from 0.65 to 0.70 for an NO_2 LUR model including wind fields. Other studies including wedge buffers as wind variables showed improvements of model performance with R^2s from 0.66 to 0.81 for biweekly NO_2 estimates in Portland, Oregon (Mavko et al., 2008) and 0.78 to 0.92 for annual NO_2 estimates in Vancouver (Ainslie et al., 2008; Su et al., 2008). In contrast to our study, where fixed site air pollution measurements were added as independent variables, Liu et al. (2012) used fixed site measurements to normalize the outcome variable (i.e. ratio of measured to fixed site NO_2). They showed that adding time and meteorology predictors to typical LUR models improved the performance considerably in different regions in Switzerland. Starting with shorter-term (i.e. biweekly) models, which could provide spatially resolved short-term estimates for health assessments, they could reduce uncertainties of estimating annual means as well. In a recent study in Sydney, adding measurements of one fixed site (but no weather data) to a biweekly NO_2 model

Table 4
Descriptive statistics of all variables used in regression model analysis.

Variable	N	Mean	Median	SD	Min	Max
Dependent variable						
Measured daily NO_2 at highway and mobile sites [μg/m^3]	1191	28.1	26.4	13.0	2.3	74.8
Independent variables (*models 1* & *2*)[a]						
Elevation over sea level [m]	8	464	461	8	456	480
Distance to highway [m]	8	168	150	145	10	450
Distance to main road [m]	8	441	501	174	147	611
Distance to railway [m]	8	317	328	150	22	518
Inverse log distance weighted light-duty traffic count on highway [vehicles per day/log(m)]	608	7903	7206	3297	667	21,319
Inverse log distance weighted heavy-duty traffic count on highway [vehicles per day/log(m)]	608	1300	1560	638	9	2252
Inverse log distance weighted light-duty traffic count on main road [vehicles per day/log(m)]	608	1084	1138	207	448	1626
Inverse log distance weighted heavy-duty traffic count on main road [vehicles per day/log(m)]	608	22	25	6	12	36
Temperature [°C]	593	9.6	9.5	7.3	−4.7	27.1
Relative humidity [%]	591	72	75	13	29	98
Stagnation index [hours per day]	588	12	13	5	0	24
Downwind frequency [hours per day]	1190	16	17	4	0	24
Air pollution measurements (*model 2*)						
Measured daily NO_2 at background site [μg/m^3]	607	22.6	20.2	11.8	1.1	66.8
Measured daily NO_x at background site [μg/m^3]	607	33.1	27.2	24.2	2.3	151.4
Measured daily ozone at highway site [μg/m^3]	592	39.7	38.2	24.6	1.7	125.0

[a] Additional variables tested: categorical land-use variable (residential area, rural area); season as categorical variable (spring = Mar–May, summer = Jun–Aug, fall = Sep–Nov, winter = Dec–Feb); weekly cycle variables sin(t) and cos(t), where $t = 2\pi \times$ date / 7.

marginally improved the performance up to an R^2 of 0.83 (Rose et al., 2010). In our study, including both time and meteorological variables as well as adding the daily background measurements increased the adjusted model R^2 even to 0.91. While the regional pollution, represented by the fixed site measurements, played a major role (partial $R^2 = 0.76$) in our rural area, it was less important in Sydney (partial $R^2 = 0.37$). In the city, the spatial variation of the traffic is much higher than in our study leading to a higher contribution of traffic predictors in the Sydney model (part. $R^2 = 0.35$ for traffic density within 50 m) compared to our model 2 (part. R^2 of 0.07 and 0.06 for log distance weighted traffic

Table 5
Regression modeling results for predicting daily NO_2 concentrations based on N = 1156 daily measurements (highway site: N = 585; 7 combined mobile sites: N = 571). (a) Model description and performance for model 1 (incl. traffic, geographic, meteorological and temporal parameters) and model 2 (model 1 plus background air pollution), (b) model validation.

(*a*) *Model performance*

Predictor variable	Estimate		SE [a]	R^2_{part} [b]	R^2_{adj} [c]
Model 1					
Stagnation index [hours per day]	1.13	*	0.04	0.25	0.70
Temperature [°C]	−0.67	*	0.03	0.20	
Inverse log distance weighted heavy-duty traffic count on highway [vehicles per day/log(m)]	8E−3	*	<0.01	0.19	
Inverse log distance weighted light-duty traffic count on highway [vehicles per day/log(m)]	3E−4	*	<0.01	0.03	
Downwind frequency [hours per day]	0.34	*	0.05	0.02	
Elevation [m]	−0.17	*	0.04	<0.01	
Weekly cycle (cos)	0.91	*	0.30	<0.01	
Weekly cycle (sin)	−0.47		0.39	<0.01	
Model 2					
Background NO_2 [μg/m^3]	0.80	*	0.02	0.76	0.91
Inverse log distance weighted light-duty traffic count on highway [vehicles per day/log(m)]	6E−4	*	<0.01	0.07	
Inverse log distance weighted heavy-duty traffic count on highway [vehicles per day/log(m)]	5E−3	*	<0.01	0.06	
Downwind frequency [hours per day]	0.22	*	0.03	0.01	
Elevation [m]	−0.19	*	0.02	0.01	
Stagnation index [hours per day]	0.19	*	0.03	<0.01	
Temperature [°C]	−0.28	*	0.02	<0.01	
Weekly cycle (sin)	0.74	*	0.21	<0.01	
Weekly cycle (cos)	0.01		0.17	<0.01	

(*b*) *Model validation*

	10-Fold cross validation			Independent validation[d]		
	R^2_{adj} [e]	RMSE [f]	Bias	R^2_{adj} [e]	RMSE [f]	Bias
Model 1	0.70	6.90	0.04 ± 6.90	0.68	3.83	−1.70 ± 4.42
Model 2	0.91	3.74	0.02 ± 3.74	0.74	4.09	−1.33 ± 4.20

* $p < 0.01$.
[a] Standard Error.
[b] Partial R^2.
[c] Adjusted model R^2.
[d] Independent validation based on 523 biweekly measurements from 10 home and 9 community outdoor sites.
[e] Adjusted validation R^2.
[f] Root mean square error.

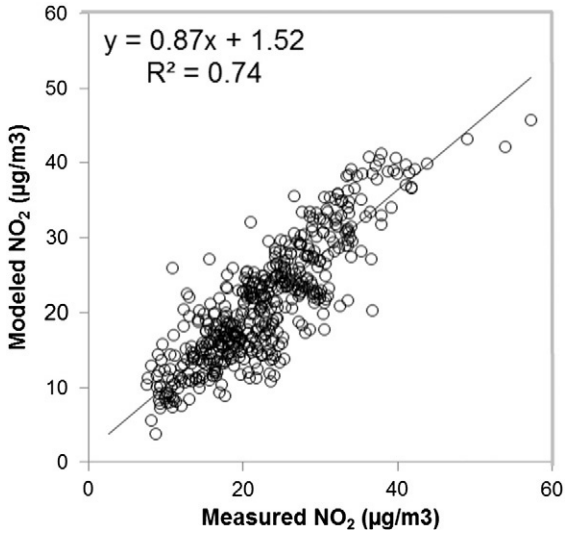


Fig. 6. Comparison between measured passive NO_2 and matched biweekly averages of modeled NO_2 (model 2) at the home and community outdoor sites. The two homes at a higher elevation were excluded.

counts). A similar approach to our model (i.e. using both, weather data and fixed site pollution measurements) was used for estimating daily black carbon in a mortality study in the Boston area (Maynard et al., 2007). However, they used non-parametric regression methods for modeling. Therefore results are not comparable to our model.

Validation of our models was done in two different ways: by cross-validation and by comparison with independent biweekly measurements at the home and community outdoor sites. Due to an uneven number of measurements among the different sites we used a 10-fold cross-validation (Hastie et al., 2001) rather than the leave-one-out cross-validation (Hoek et al., 2008). For both models, calculated cross-validation R^2s were equal to their model performance R^2s (Table 5b). However, root mean square error (RMSE) and bias were smaller for model 2 (Table 5b).

For the independent validation we compared the passively measured biweekly NO_2 concentrations at the children's homes and community outdoor sites with matched biweekly averages of the predicted NO_2 concentrations from the models. From 166 expected home outdoor measurements six samples were void due to mishandling and six tubes got lost. Measurements from one home (N = 17) were excluded for the analysis due to unrealistic levels compared to nearby home and mobile sites. The precision of the passive sampler

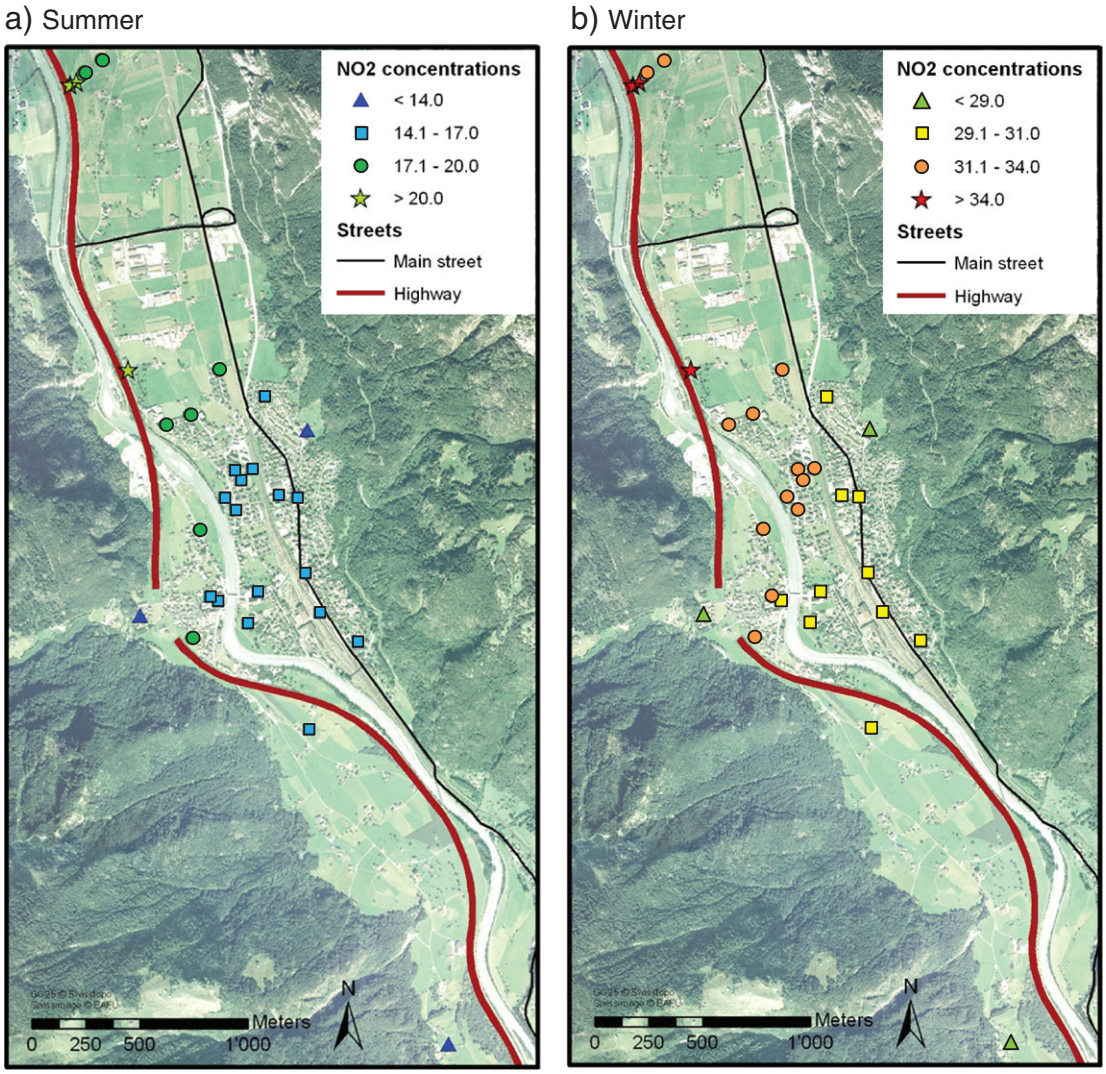


Fig. 7. Distribution of predicted NO_2 (model 2) in the valley in a) summer (June–August), and b) winter (December–February) 2008.

was 3.8% and the mean difference was 0.8 ± 1.1 μg/m^3 (N = 89 pairs) which is in agreement with previous studies (Liu et al., 2012). All field blanks were below the analytical detection limit of 0.4 μg/m^3 (N =37). NO_2 concentrations from passive samplers agreed very well with the collocated continuous measurements with slope = 0.93 and intercept = 2.4 μg/m^3 (R^2 = 0.91, N = 114). Our final models underperformed for two of the children's homes located about 120 and 580 m above the valley because measurements used to construct the models were only taken at the bottom of the valley. Model estimates for the other 10 homes (N = 120) and 9 community outdoor sites (N = 403) matched very well with the passive sampler measurements with overall R^2s of 0.68 and 0.74 and mean bias of −1.7 ± 4.4 μg/m^3 and −1.3 ± 4.2 μg/m^3 for models 1 and 2, respectively (Table 5, Fig. 6). Considering the difference in measurement methods (passive method underestimating NO_2 by 9%), the agreement would in fact be even better. Comparison with the biweekly passive measurements also showed a considerable reduction in exposure misclassification using model 2 estimates (R^2 = 0.74, slope = 0.87) instead of model 1 estimates (R^2 = 0.72, slope = 0.68) or just the background measurements (R^2 = 0.55, slope = 0.72), which will be important for the health analysis in the panel study.

Fig. 7 shows mean NO_2 levels predicted for all sites in Erstfeld in summer and winter using model 2. Winter estimates were 1.5 to 2 times higher than in summer. As expected, the highest concentrations were estimated very close to the highway. The spatial distribution was more homogeneous in winter due to general lower wind speeds and frequent inversion episodes which trapped the pollution within the residential area. This discrepancy of spatial variation in different seasons was also shown in previous studies (Liu et al., 2012). Pollutant levels for the houses at the side of the valley were lowest due to their elevated location. Generally, air pollution levels are highest near the valley floor where the sources are located and decrease with increasing elevation (Gohm et al., 2009). Air pollution levels at sites directly on the main road were underestimated (bias between −6.5 and −2.8 μg/m^3), because main road related variables did not enter the model. Underestimation was larger in summer (bias: −9.4 to −4.6 μg/m^3) than in winter (bias: −3.9 to −3.4 μg/m^3).

Because 50% of our modeling data was collected at the highway site, we performed a sensitivity analysis for the final model 2 by excluding the highway data in the training set. There was no influence on the adjusted R^2, nor did variable estimates change substantially, except for downwind frequency (from 0.22 to 0.07).

With this unique model, we were able to make quite robust short-term NO_2 estimates (at all locations within the village) that are being used for assessment of acute (i.e. daily) health effects (will be reported separately). The large number of additional measurements in the village also allowed us to independently validate our model. However, one of the limitations of the model was its inapplicability to elevated locations in the valley. A vertical profile with complex pollution distribution, as described in Gohm et al. (2009), was not possible due to missing contrast in elevation of our measuring sites. Not having a true background site was another limitation of this study. Because of the strong influence of the highway traffic on the chosen background site, model 2 cannot assess the total actual contribution from the highway but only the distance-dependent incremental local concentrations attributable to the highway traffic. Being aware of this limitation the model captures though very well the spatial variation within the residential area on the grounds of the Alpine valley.

4. Conclusions

Our study confirmed the substantial spatial variability of traffic related air pollutants such as NO_2, EC and particulate number with proximity to the highway. Within only 150–200 m, concentrations of these pollutants decay ~30–40% to background levels. All pollutants followed the daily trend of the heavy-duty traffic counts even though trucks accounted for only 14% of the total traffic. This evidence is important for policy regarding traffic regulations on national and international levels. We also provided a way to model spatially resolved short-term exposure to NO_2 by enhancing LUR models with short term traffic, meteorological and fixed site pollution data. The model performed very well (explaining over 90% of outdoor NO_2 variability) and agreed well with independent measurements (R^2 = 0.74). These daily estimates will allow us to assess acute health effects of highway traffic air pollution in our panel study.

Conflict of interest

The authors declare they have no competing financial interests.

Acknowledgments

This work was funded by the Federal Office for the Environment (FOEN) of the Swiss Government (No. 050303/G161-1955). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the FOEN. We would like to thank Peter Boehler and Raffael Kaenzig from inNET Monitoring AG (Altdorf, Switzerland) for providing the extensive air pollution data. We are also grateful to Dr. Andrea Fischer at Empa (Dübendorf, Switzerland) for providing the conversion factors for EC and OC.

We would like to dedicate this paper to (late) Prof. Dr. Lee-Jane Sally Liu, who passed away in June 2011. We are deeply grateful for her supervision and guidance throughout the study and she still remains our constant inspiration.

References

Ainslie B, Steyn DG, Su J, Buzzelli M, Brauer M, Larson T, et al. A source area model incorporating simplified atmospheric dispersion and advection at fine scale for population air pollutant exposure assessment. Atmos Environ 2008;42:2394–404.

Arain MA, Blair R, Finkelstein N, Brook JR, Sahsuvaroglu T, Beckerman B, et al. The use of wind fields in a land use regression model to predict air pollution concentrations for health exposure studies. Atmos Environ 2007;41:3453–64.

BAFU. NABEL — Luftbelastung 2008. Messresultate des Nationalen Beobachtungsnetzes für Luftfremdstoffe (NABEL). Nr. 0919. Umwelt-Zustand. Bern: Bundesamt für Umwelt (BAFU); 2009.

Cavalli F, Viana M, Yttri KE, Genberg J, Putaud J-P. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos Meas Tech 2010;3:79–89.

de Franceschi M, Zardi D. Study of wintertime high pollution episodes during the Brenner-South ALPNAP measurement campaign. Meteorol Atmos Phys 2008;103:237–50.

EEA. EMEP/EEA air pollutant emission inventory guidebook. Copenhagen: European Environment Agency (EEA); 2009.

Federal Office of Transport. Freight traffic and transport crossing the Swiss Alps 2010. Berne www.bav.admin.ch 2011.

Fruin S, Westerdahl D, Sax T, Sioutas C, Fine PM. Measurements and predictors of on-road ultrafine particle concentrations and associated pollutants in Los Angeles. Atmos Environ 2008;42:207–19.

Gauderman WJ, Vora H, McConnell R, Berhane K, Gilliland F, Thomas D, et al. Effect of exposure to traffic on lung development from 10 to 18 years of age: a cohort study. Lancet 2007;369:571–7.

Gehrig R, Hill M, Imhof D, Weingartner E, Baltensperger U. Separate determination of PM_{10} emission factors of road traffic for tailpipe emissions and emissions from abrasion and resuspension processes. Int J Environ Pollut 2004;22:312–25.

Gohm A, Harnisch F, Vergeiner J, Obleitner F, Schnitzhofer R, Hansel A, et al. Air pollution transport in an alpine valley: results from airborne and ground-based observations. Boundary Layer Meteorol 2009;131:441–63.

Goswami E, Larson T, Lumley T, Liu L-JS. Spatial characteristics of fine particulate matter: identifying representative monitoring locations in Seattle, Washington. J Air Waste Manage 2002;52:324–33.

Harnisch F, Gohm A, Fix A, Schnitzhofer R, Hansel A, Neininger B. Spatial distribution of aerosols in the Inn Valley atmosphere during wintertime. Meteorol Atmos Phys 2008;103:223–35.

Hastie T, Tibshirani R, Friedman J. The elements of statistical learning data mining, inference, and prediction. Springer series in statistics. Springer; 2001.

Hazenkamp-von Arx M, Schindler C, Ragettli M, Kunzli N, Braun-Fahrlander C, Liu S L-J. Impacts of highway traffic exhaust in alpine valleys on the respiratory health in adults: a cross-sectional study. Environ Health 2011;10:13.

HEI (Health Effects Institute). HEI panel on the health effects of traffic-related air pollution. Traffic-related air pollution: a critical review of the literature on emissions, exposure, and health effects. 17. Boston: Health Effects Institute; 2010 (Available at: http://pubs.healtheffects.org/view.php?id=334).

Hoek G, Beelen R, de Hoogh K, Vienneau D, Gulliver J, Fischer P, et al. A review of land-use regression models to assess spatial variation of outdoor air pollution. Atmos Environ 2008;42:7561–78.
Jerrett M, Arain A, Kanaroglou P, Beckerman B, Potoglou D, Sahsuvaroglu T, et al. A review and evaluation of intraurban air pollution exposure models. J Expo Anal Environ Epidemiol 2004;15:185–204.
Kelly FJ, Fussell JC. Air pollution and airway disease. Clin Exp Allergy 2011;41:1059–71.
Kuenzli N, Perez L, Rapp R. Air quality and health. Lausanne, Switzerland: ERS; 2010.
Liu SL-J, Curjuric I, Keidel D, Heldstab J, Künzli N, Bayer-Oglesby L, et al. Characterization of source-specific air pollution exposure for a large population-based Swiss cohort (SAPALDIA). Environ Health Perspect 2007;115:1638–45.
Liu SL-J, Tsai M-Y, Keidel D, Gemperli A, Ineichen A, Hazenkamp-von Arx M, et al. Long-term exposure models for traffic related NO_2 across geographically diverse areas over separate years. Atmos Environ 2012;46:460–71.
Mavko ME, Tang B, George LA. A sub-neighborhood scale land use regression model for predicting NO_2. Sci Total Environ 2008;398:68–75.
Maynard D, Coull BA, Gryparis A, Schwartz J. Mortality Risk Associated with Short-Term Exposure to Traffic Particles and Sulfates. Environ Health Perspect 2007;115:751–5.
Norris G, Larson T, Koenig J, Claiborn C, Sheppard L, Finn D. Asthma aggravation, combustion, and stagnant air. Thorax 2000;55:466–70.
Oliveira MLM, Silva CM, Moreno-Tost R, Farias TL, Jiménez-López A, Rodríguez-Castellón E. Modelling of NOx emission factors from heavy and light-duty vehicles equipped with advanced aftertreatment systems. Energy Convers Manage 2011;52:2945–51.
Padró-Martínez LT, Patton AP, Trull JB, Zamore W, Brugge D, Durant JL. 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;61:253–64.
Putaud J-P, Van Dingenen R, Alastuey A, Bauer H, Birmili W, Cyrys J, et al. A European aerosol phenomenology — 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos Environ 2010;44:1308–20.
Rose N, Cowie C, Gillett R, Marks GB. Validation of a spatiotemporal land use regression model incorporating fixed site monitors. Environ Sci Technol 2010;45:294–9.
Schäfer K, Vergeiner J, Emeis S, Wittig J, Hoffmann M, Obleitner F, et al. Atmospheric influences and local variability of air pollution close to a motorway in an Alpine valley during winter. Meteorol Z 2008;17:297–309.
Schnitzhofer R, Norman M, Wisthaler A, Vergeiner J, Harnisch F, Gohm A, et al. A multimethodological approach to study the spatial distribution of air pollution in an Alpine valley during wintertime. Atmos. Chem. Phys. 2009;9:3385–96.
Su JG, Brauer M, Ainslie B, Steyn D, Larson T, Buzzelli M. An innovative land use regression model incorporating meteorology for exposure analysis. Sci Total Environ 2008;390:520–9.
Subramanian R, Khlystov AY, Robinson AL. Effect of peak inert-mode temperature on elemental carbon measured using thermal–optical analysis. Aerosol Sci Tech 2006;40:763–80.
Westerdahl D, Fruin S, Sax T, Fine PM, Sioutas C. Mobile platform measurements of ultrafine particles and associated pollutant concentrations on freeways and residential streets in Los Angeles. Atmos Environ 2005;39:3597–610.
Zhu Y, Hinds WC, Kim S, Shen S, Sioutas C. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. Atmos Environ 2002;36:4323–35.

3. Sources of PM_{10}

Article 3: PM10 source apportionment in a Swiss Alpine valley impacted by highway traffic

Regina E. Ducret-Stich[1,2], Ming-Yi Tsai[1,2,3], Devraj Thimmaiah[1], Nino Kuenzli[1,2], Philip K. Hopke[4], Harish C. Phuleria[1,2]

[1] Department of Epidemiology and Public Health, Swiss Tropical and Public Health Institute, Socinstrasse 57, 4002 Basel, Switzerland

[2] University of Basel, 4003 Basel, Switzerland

[3] Department of Environmental & Occupational Health Sciences, University of Washington, Seattle, WA 98195 USA

[4] Department of Chemical Engineering, Clarkson University, Potsdam, New York, USA

This article has been published in the journal Environmental Science and Pollution Research

Environ Sci Pollut Res (2013) 20:6496–6508
DOI 10.1007/s11356-013-1682-1

RESEARCH ARTICLE

PM_{10} source apportionment in a Swiss Alpine valley impacted by highway traffic

Regina E. Ducret-Stich · Ming-Yi Tsai · Devraj Thimmaiah · Nino Künzli · Philip K. Hopke · Harish C. Phuleria

Received: 22 December 2012 / Accepted: 26 March 2013 / Published online: 23 April 2013

Abstract Although trans-Alpine highway traffic exhaust is one of the major sources of air pollution along the highway valleys of the Alpine regions, little is known about its contribution to residential exposure and impact on respiratory health. In this paper, source-specific contributions to particulate matter with an aerodynamic diameter < 10 μm (PM_{10}) and their spatio-temporal distribution were determined for later use in a pediatric asthma panel study in an Alpine village. PM_{10} sources were identified by positive matrix factorization using chemical trace elements, elemental, and organic carbon from daily PM_{10} filters collected between November 2007 and June 2009 at seven locations within the village. Of the nine sources identified, four were directly road traffic-related: traffic exhaust, road dust, tire and brake wear, and road salt contributing 16 %, 8 %, 1 %, and 2 % to annual PM_{10} concentrations, respectively. They showed a clear dependence with distance to highway. Additional contributions were identified from secondary particles (27 %), biomass burning (18 %), railway (11 %), and mineral dust including a local construction site (13 %). Comparing these source contributions with known source-specific biomarkers (e.g., levoglucosan, nitro-polycyclic aromatic hydrocarbons) showed high agreement with biomass burning, moderate with secondary particles (in winter), and lowest agreement with traffic exhaust.

Keywords Source apportionment · PMF · Highway traffic · PM10 · Swiss Alpine valley · Levoglucosan · NitroPAH

We would like to dedicate this paper to the late Prof. Lee-Jane Sally Liu, who passed away in June 2011. We are deeply grateful for her supervision and guidance throughout the study, and she still remains a constant inspiration.

Responsible editor: Gerhard Lammel

Electronic supplementary material The online version of this article (doi:10.1007/s11356-013-1682-1) contains supplementary material, which is available to authorized users.

R. E. Ducret-Stich (✉) · M.-Y. Tsai · D. Thimmaiah · N. Künzli · H. C. Phuleria
Department of Epidemiology and Public Health, Swiss Tropical and Public Health Institute, Socinstrasse 57, P.O. Box, 4002, Basel, Switzerland
e-mail: regina.ducret@unibas.ch

R. E. Ducret-Stich · M.-Y. Tsai · N. Künzli · H. C. Phuleria
University of Basel, Petersplatz 1, 4003 Basel, Switzerland

M.-Y. Tsai
Department of Environmental and Occupational Health Sciences, University of Washington, Box 357234, Seattle, WA 98195, USA

P. K. Hopke
Department of Chemical and Biomolecular Engineering and Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam, NY 13699-5708, USA

Introduction

Inhalable particulate matter consists of a complex mixture of particles and droplets of varying size and composition. They originate from different natural and anthropogenic sources, e.g., fires, windblown dust, motor vehicles, power plants, construction activities, and contain primary and secondary particles (Seinfeld and Pandis 2006). Although there is considerable evidence that airborne particulate matter (PM) is associated with adverse respiratory and cardiovascular health effects (Davidson et al. 2005; Pope and Dockery 2006; Russell and Brunekreef 2009; US EPA 2009), only few studies have examined association of apportioned components and sources of PM with health outcomes (Stanek et al. 2011).

From a policy point of view, it is crucial to identify air pollution sources that have the greatest impact on public health in order to apply targeted emission management

strategies. For example, emission regulations are continuously tightened for traffic exhaust, one of the most investigated sources (Brugge et al. 2007; Health Effects Institute 2010). However, there is increasing evidence of health impacts from other sources such as biomass burning (Laumbach and Kipen 2012; Naeher et al. 2007) or Saharan dust events (Karanasiou et al. 2012). Therefore, application of receptor modeling has become more and more important in recent years for estimating the exposure from the different sources (Hopke 2003; Viana et al. 2008).

Due to health concerns raised in communities along the main north–south transit route crossing the Alps (Hazenkamp-von Arx et al. 2011), Swiss Federal Office for the Environment funded this pediatric asthma panel study to investigate the health impact of short-term air pollution from local sources. The primary north–south transit corridor study (Hazenkamp-von Arx et al. 2011) comprised of ten communities along the Swiss Alpine highway corridors including Erstfeld, a village located in a narrow and flat Alpine valley bordered by steep mountain slopes along the Swiss transit highway A2. The focus of the current study is the chemical composition of PM in this village. One and a half years of air pollution measurements, at several sites within the village, were used to analyze the temporal and spatial distribution of the different pollutants (Ducret-Stich et al. 2013). Traffic-related pollutants such as nitrogen dioxide (NO_2), elemental carbon (EC) and particle number concentration were highly heterogeneous in space (i.e., decreasing concentrations with increasing distance to the highway). In contrast, particulate matter with an aerodynamic diameter <10 μm (PM_{10}) and organic carbon (OC) influenced also by sources other than traffic, showed a more homogeneous spatial distribution.

The aim of this paper is to find and apportion the main sources contributing to the total PM_{10} in Erstfeld using positive matrix factorization (PMF). Single sources such as traffic exhaust, biomass burning, and secondary pollutants are validated by comparison with source-specific biomarkers (e.g., levoglucosan, nitro-polycyclic aromatic hydrocarbons). We describe the spatial and temporal distribution of the source-specific contributions, with special focus on highway-related sources. The modeled source-specific contribution estimates are subsequently being used to assess acute respiratory health effects in school children.

Methods

Study description

From November 2007 to June 2009, several air pollutants were measured in Erstfeld, a village with about 3,800 inhabitants located in an 800 to 900 m wide Alpine valley in Switzerland. A detailed description of the study region, monitoring sites, and measured pollutants can be found elsewhere (Ducret-Stich et al. 2013). Daily PM_{10} filters were concurrently collected at one fixed highway and one mobile station, which was moved each month to one of the seven locations (Fig. 1). The highway site was situated north of the village right beside the highway (22 m from the centerline). From that location, three mobile sites were additionally located at perpendicular distances of 55, 102, and 198 m to the highway (Fig. 1, sites 1–3). The other four mobile sites were chosen to represent the residential area and to capture the impact of additional sources such as the main road and railways (Fig. 1, sites 4–7). The mobile station measurements were scheduled to cover all seasons for each mobile station in the residential area during the

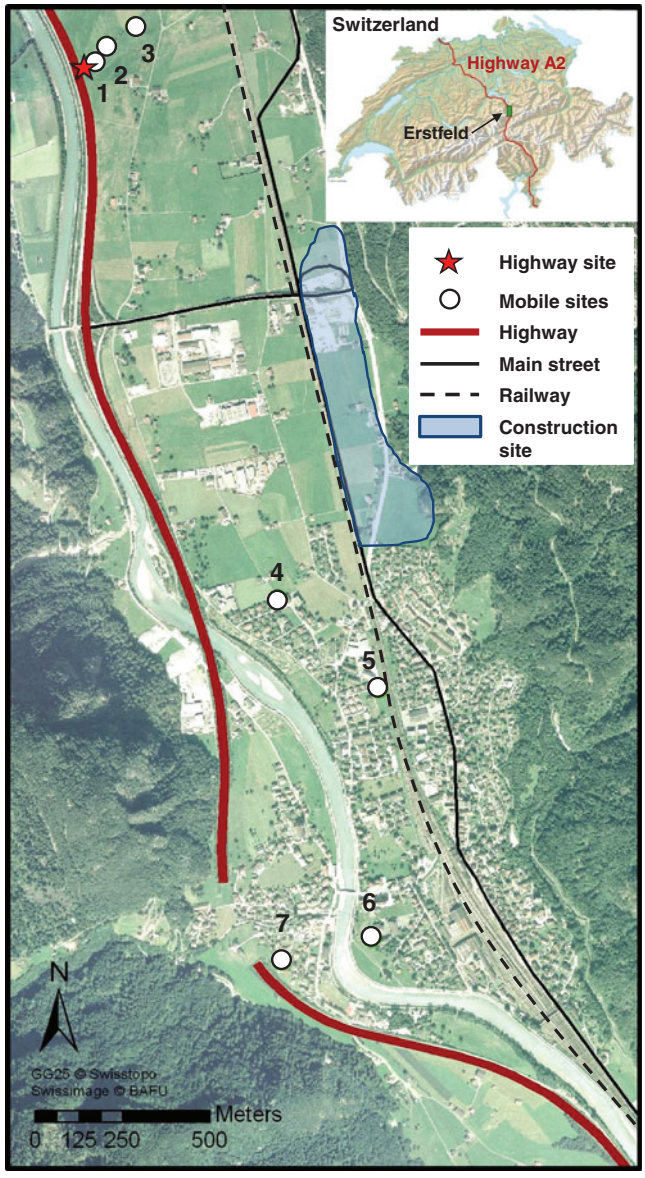


Fig. 1 Map of Erstfeld with measurement sites

study. During the whole study period there was a major construction site north-east of site 4 (Fig. 1), where the largest train tunnel in the world, the base tunnel through the Gotthard mountain (Alp Transit), is still being built.

Sampling methods

At the highway and mobile sites, high volume samplers (Digitel DHA-80) with a flow rate of 30 m^3/h were used to collect concurrent 24-h PM_{10} on 150 mm quartz fiber filters (Pallflex Tissuquartz 2500QAT-UP, Pall AG, Switzerland). At the mobile sites, 24-h PM_{10} was additionally collected on 47 mm Teflon filters (PTFE 2.0 μm pore size, Blanc-Labo S.A., Switzerland) using a Partisol low volume sampler (Partisol®-Plus Modell 2025 Sequential Air Sampler, Thermo Fisher Scientific) with a flow rate of 1 m^3/h. All filters were pre-weighted and pre-conditioned (48 h at 22 °C and 50 % RH), and their mass concentrations were determined by standard gravimetric methods. The limit of detection, determined as three times the standard deviation of the field blanks, was 2.3 μg/m^3 (N=57) and 2.4 μg/m^3 (N=30) for the quartz- and Teflon-filters, respectively. The two measurement methods (high volume versus Partisol) agreed very well with an R^2 of 0.93 (slope=0.96; intercept=−1.78 μg/m^3) and a mean difference of 1.12± 2.86 μg/m^3 (N=521).

Chemical analysis

All of the quartz fiber filters were analyzed for EC and OC using a thermal–optical transmission method (TOT, OCEC Analyzer Sunset Laboratory Inc.). Due to a protocol change in 2009, the filters were analyzed with two different temperature profiles. Filters from 2007/2008 were analyzed with the NIOSH700$^+$ protocol, while filters from 2009 were analyzed with the EUSAAR2 protocol, details of the protocols are described separately (Ducret-Stich et al. 2013). Since the two protocols provided different EC–OC fractions, it was not possible to use the fractionated EC–OC data without losing a substantial portion of the data (>30 % corresponding to 2009 measurements). Thus, we used total EC and OC and adjusted the NIOSH700+ concentrations to levels of the EUSAAR2 protocol with the following factors derived from orthogonal regression analysis of 102 ambient filters analyzed with both protocols (Ducret-Stich et al. 2013):

$$EC_{EUSAAR2} = 1.10 \times EC_{NIOSH700+} \quad (1)$$

$$OC_{EUSAAR2} = 0.92 \times OC_{NIOSH700+} \quad (2)$$

The Teflon filters at the mobile sites were used to determine concentrations of 48 chemical elements (Table 1 and Online Resource Table S1) by energy-dispersive X-ray fluorescence (XRF) (Cooper Environmental Services LLC, Portland, OR, USA). After the non-destructive XRF analysis, PM was extracted from the filters using Dichloromethane (CH_2Cl_2) (Miller-Schulze et al. 2010) and combined into 1- and 2-week composites for analysis of three nitropolycyclic aromatic hydrocarbons (NPAHs) and levoglucosan (LG), respectively. NPAHs were analyzed with two-dimensional high-performance liquid chromatography tandem mass spectrometry (Miller-Schulze et al. 2010) and included 1-nitropyrene (1-NP), a diesel marker (Albinet et al. 2007; Ringuet et al. 2012b; Scheepers et al. 1995), and 2-nitropyrene (2-NP) and 2-nitrofluoranthene (2-NFl), two markers for secondary pollution (Arey et al. 1967; Ringuet et al. 2012a, b; Sweetman et al. 1967). The wood smoke marker LG (Jordan et al. 2006; Simoneit et al. 1999) was analyzed by gas chromatography/mass spectrometry as described in Simpson et al. (2004).

Table 1 Summary statistics, method detection limit (MDL), % of data below MDL, signal-to-noise ratio (S/N), and PMF category of all species which were used for PMF analysis (N=510)

Species	Mean (ng/m^3)	SD (ng/m^3)	MDL (ng/m^3)	% below MDL	S/N	PMF category
PM_{10}	15,490	9,732	2,400	0	0.8	Weak
MM[a]	3,030	3,944			0.7	Weak
EC	1,112	706	51	1	3.0	Strong
OC	2,761	1,587	476	2	2.1	Strong
Al	132	232	1.63	5	25.9	Strong
Ba	5.98	7.21	0.77	25	2.4	Weak
Br	1.77	1.07	0.29	4	8.3	Weak
Ca	340	319	0.48	0	26.3	Strong
Cl	85	172	1.73	44	25.5	Strong
Cr	3.86	3.76	0.34	3	11.9	Strong
Cu	12	10	0.43	0	20.3	Weak
Fe	975	1,024	0.48	0	26.6	Strong
K	352	281	1.10	0	26.4	Strong
Mg	32	51	2.02	22	10.4	Strong
Mn	13	11	0.43	0	20.9	Strong
Na	24	55	7.82	75	5.6	Weak
Ni	0.65	0.74	0.34	45	2.8	Strong
Pb	4.75	4.65	0.48	9	12.3	Weak
Rb	1.04	0.79	0.34	19	3.8	Strong
S	606	457	0.53	0	27.1	Strong
Si	442	625	1.20	0	26.9	Strong
Ti	14	21	0.29	3	19.1	Strong
V	0.60	0.69	0.29	42	1.4	Weak
Zn	21	15	0.58	0	22.6	Strong

For summary of all other species see Online Resource Table S1

[a] Missing mass

Mass closure

A mass closure analysis was performed on the data by comparing the reconstructed mass (RCM) with the measured mass. To calculate the RCM, the following estimates were used:

$$\mathrm{OM} = 1.6[\mathrm{OC}] \tag{3}$$

$$\mathrm{Sulfate} = 4.125[\mathrm{S}] \tag{4}$$

$$\begin{aligned}\mathrm{Mineral\ dust} = {} & 2.14[\mathrm{Si}] + 1.89[\mathrm{Al}] + 1.66[\mathrm{Mg}] \\ & + 1.40\left[\mathrm{Ca_{geo}}\right] + 1.21\left[\mathrm{K_{geo}}\right] \\ & + 1.43\left[\mathrm{Fe_{geo}}\right]\end{aligned} \tag{5}$$

$$\begin{aligned}\mathrm{RCM} = {} & [\mathrm{EC}] + \mathrm{OM} + \mathrm{Sulfate} + \mathrm{Mineral\ dust} \\ & + \sum \text{anthropogenic part of Ca, K, Fe} \\ & + \sum \text{all other species}\end{aligned} \tag{6}$$

where [ ] represent the concentration of the specific element. Organic matter (OM) (Eq. 3) is accounting for the mass of oxygen and other unmeasured elements in non-carbon organic matter (Turpin and Lim 2001). Although Turpin and Lim recommended a multiplication factor larger than 1.6 for non-urban areas, we used 1.6 because of the impact from the highway traffic on the air pollution in this valley (Ducret-Stich et al. 2013). In Eq. 4, the ratio of the atomic weights of ammonium sulfate ($(NH_4)_2SO_4$) and Sulfur (S) is used assuming all the sulfate is fully neutralized and occurs on the Teflon filter as ammonium sulfate. For mineral dust (Eq. 5), the elements are assumed to be present as oxides (Chow et al. 1994). However, as anthropogenic sources also emit calcium (Ca), potassium (K), and iron (Fe), only the geogenic part of these elements were used, i.e., $Ca_{geo}=1.15[Al]$, $K_{geo}=0.61[Al]$, and $Fe_{geo}=1.13[Al]$ (Gianini et al. 2012b).

RCM, as defined in Eq. 6, explained on average 76 % (SD=12 %) of the measured mass (Online Resource Fig. S2). As our OM estimate (Eq. 3) was rather conservative (Turpin and Lim 2001), the missing mass (MM), defined as measured mass minus RCM, also contained the organic mass not accounted for in Eq. 6. In addition, RCM did not include nitrates, which were not measured in this study. Because MM showed higher concentrations in winter, MM was assumed to represent nitrates, which are mostly present as ammonium nitrate (NH_4NO_3) and readily form and persist in cold temperature environments (Seinfeld and Pandis 2006). MM, with an average of 24 % PM_{10} mass, was also comparable to secondary nitrate contributions to PM_{10} in other Swiss regions (22–32 %) (Gianini et al. 2012a). Therefore, we included the MM as an additional "species" representing nitrates and additional organic matter in the source apportionment analysis.

Receptor modeling

To find and apportion the different sources of PM_{10}, we used the PMF software from the U.S. Environmental Protection Agency (EPA PMF 3.0). PMF is a receptor model, which solves a positively constrained bilinear mass balance model based on a weighted least-squares fit (Paatero 1997; Paatero and Tapper 1994).

Database construction

Chemical species with a large fraction (>50 %) of concentrations below the method detection limit (MDL) were excluded from the analysis (Online Resource Table S1), except sodium (Na), which was included as a tracer for road salt. Arsenic (As) was excluded due to weak signals where only 31 % of the concentrations were above three times the MDL. Most species with an atomic number above 40 (zirconium (Zr)) except for lead (Pb), and barium (Ba) were excluded because of the difficulties in XRF analysis. Phosphorus (P) was also excluded as it is generally a poor variable in XRF analysis due to the influence of the large Sulfur (S) peak that is adjacent in the X-ray spectrum. The final data included 24 species (Table 1).

Concentrations and uncertainties of the chemical species data were processed according to Polissar et al. (1998) for the PMF analysis. Values below the MDL were replaced by half of the MDL values, and their uncertainties were set to 5/6 of the MDL values. There were no missing values in our data set. For EC and OC, the uncertainties were set to the sum of ½ of the minimum measured value of all samples (EC, 0.01 μg/m^3; OC, 0.12 μg/m^3) plus instrument detection limit obtained from the manufacturer (0.04 μg/m^3) plus MDL, defined as three times the standard deviation of the field blanks calculated for each set of blanks (2007/2008 data (NIOSH700+) and 2009 data (EUSAAR2)) (e-CFR, 2012). The uncertainty in the MM was calculated as the square root of the sum of the variances of all measured species and measured mass (Wu et al. 2007). PM_{10} was additionally included as an independent variable into the PMF model to directly obtain the source contributions to the daily PM_{10} mass concentrations. It is assigned a high uncertainty of four times the value to decrease its weight in the model fit (Kim et al. 2003b). Uncertainty of species with a signal-to-noise ratio (S/N)<2 (PM_{10}, MM, vanadium (V)) were increased by a factor of three by categorizing them as "weak" in the PMF analysis (Norris et al. 2008; Paatero and Hopke 2003). Also Na, Ba, and Pb were set to weak to

account for their poor data quality described above. In addition, bromine (Br) and copper (Cu) were categorized as weak to reduce the number of scaled residuals>±3 (Norris et al. 2008; Paatero and Hopke 2003).

Unusual events can distort the results of source profiles and contributions (Norris et al. 2008); therefore, 19 of 529 samples were excluded from our analysis due to: fireworks (high Ba and K, N=3); two Saharan dust events in May and October 2008 (high PM_{10}, silicon (Si), magnesium (Mg), aluminum (Al), titanium (Ti), N=6); possible local events from the construction site (high Si, Mg, Al, Ti, N=6); local road salt spreading (very high Na and chlorine (Cl), N=1); and three unexplained local events with high Pb, zinc (Zn); high Ba, K, molybdenum (Mo); and high P, respectively. Summary statistics of the final 510 samples included in the PMF analysis are provided in Table 1.

Model execution

PMF was run in the robust mode for seven to ten sources using all 510 samples together. To determine the final number of sources, the distribution of the scaled residuals was examined to ensure the data were properly fitted. The extracted profiles were compared with profiles from the literature. This combination of tests was used to identify the most physically reasonable solution. The best results were found for nine sources. For up to eight sources, the residuals were positively skewed and with ten sources the tire and brake wear factor split into two unrecognizable factors. The model uncertainty was tested with bootstrapping (100 runs) (Norris et al. 2008). All factors were mapped to a base factor in every run, indicating a stable result.

PMF does not generally produce a unique solution due to rotational ambiguity (Paatero et al. 2002). Therefore, PMF solutions were systematically explored by varying the Fpeak parameter between −1 and +1 to find Fpeak–intervals for which the penalty function Q(E) values remained relatively constant (Norris et al. 2008; Paatero et al. 2002). For these intervals, PMF solutions were analyzed using *G space plotting* to investigate statistical dependence between source contributions caused by unrealistic rotations (Paatero et al. 2005). An Fpeak value of −0.2 was found to give the best results after comparing the *G space* plots and source profiles. For Fpeak=0 several profiles displayed unrealistic values as shown in Online Resource Fig. S3.

Validation of the final PMF solution was done by regressing the predicted PM_{10} (sum of all source contributions from PMF) with the measured PM_{10} which resulted in an R^2 of 0.87 (Fig. 2). However, an increasing dispersion around the regression line was observed for higher mass values measured mainly in winter (Fig. 2). This might be caused by the underestimation of the organic matter in winter and/or some loss of semi-volatile material on the filters due to temperature changes before weighing. The

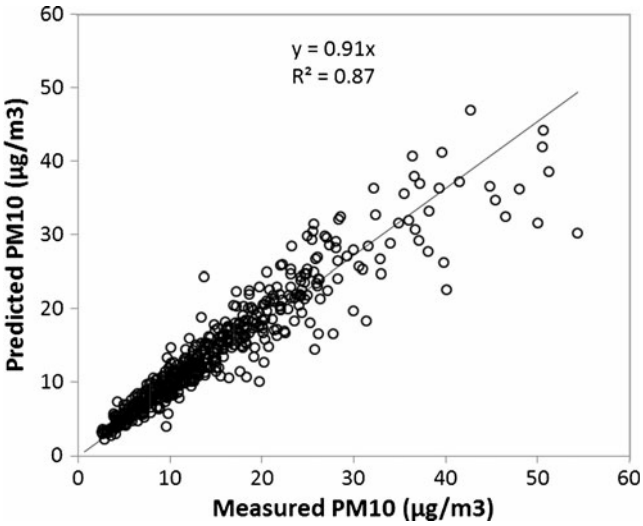


Fig. 2 Comparison of measured PM_{10} concentrations versus PMF predictions

PMF solution was additionally validated using measurements of the biomarkers levoglucosan and NPAHs to further compare source-specific contributions from biomass burning, traffic exhaust, and secondary pollution.

Results and discussion

Source profiles

We identified nine sources of which four were directly traffic-related, namely, traffic exhaust, road dust, tire and brake wear, and road salt (Fig. 3). Traffic was also indirectly related to secondary particles by producing some of their precursors. Other sources were biomass burning, railway, and two mineral-related sources, mineral dust, and minerals from the construction site (Fig. 4).

Traffic exhaust

The traffic exhaust profile was dominated by EC and OC with some contributions of abrasion-related metals such as Zn, Ba, and Cu (Schauer et al. 2006) (Fig. 3a). Source contributions were higher on weekdays than on weekends. This result corresponded to the higher weekday traffic counts of heavy duty trucks (with lower counts on weekends due to a Sunday truck traffic ban) than to the total traffic, which showed higher counts on weekends (Ducret-Stich et al. 2013) (Online Resource Fig. S4b). Although this relationship seemed to point to a strong correlation between attributed traffic exhaust PM_{10} and diesel-powered heavy duty trucks, comparison with the diesel marker, 1-NP, showed only an R^2 of 0.13 (Fig. 5a). A higher correlation was obtained with the more general traffic marker NO_2 (R^2=0.50) (Fig. 5b). In contrast to daily

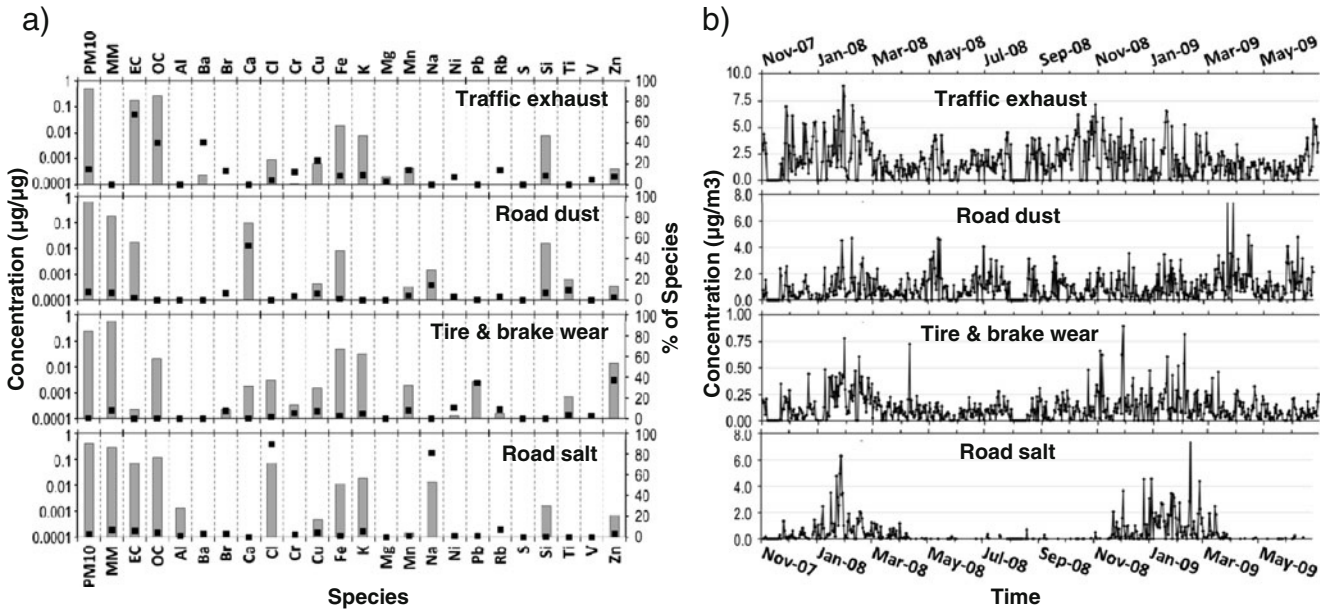


Fig. 3 Attributed sources directly related to traffic: **a** PM_{10} source profiles (*solid bars, left axis*) with explained variation (*squares, right axis*) and **b** daily PM_{10} source contributions. *Left axis* in source profiles describes the normed concentration such that the sum of all elemental contribution within a factor equals 1

NO_2 measurements, 1-NP was only available as weekly average concentrations. Moreover, filter reaction artifacts during sampling may have resulted in overestimation of 1-NP and thus to the low correlation with traffic exhaust PM_{10}. Reported EC/OC ratios for gasoline and diesel vehicle emissions typically range between 0.1 to 0.5 and 1.0 to 4.0, respectively (Liu et al. 2006; Lough et al. 2007). The EC/OC ratio of 0.7 in our study reflected the mixed traffic fleet with about 14 % of heavy duty vehicles (diesel) and 86 % passenger cars of which about 18 % used diesel.

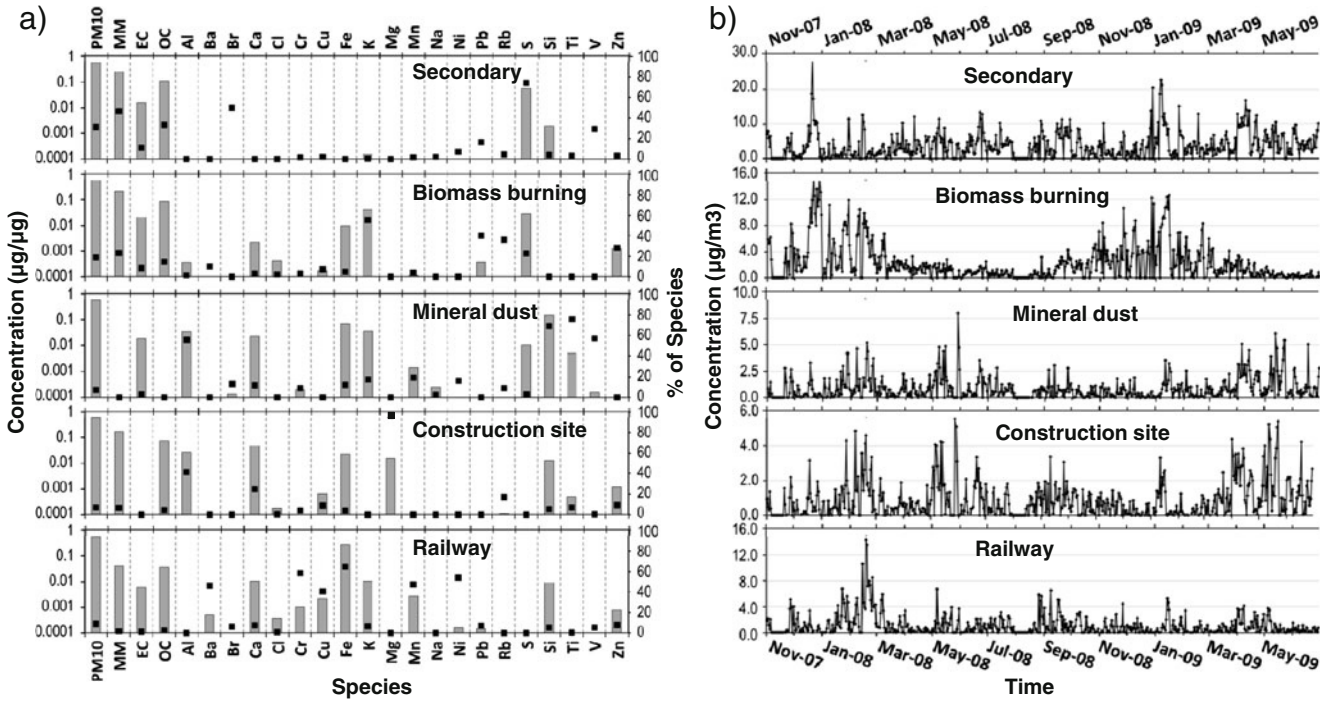


Fig. 4 Attributed sources not directly related to traffic: **a** PM_{10} source profiles (*solid bars*, *left axis*) with explained variation (*squares, right axis*) and **b** daily PM_{10} source contributions. *Left axis* in source profiles describes the normed concentration such that the sum of all elemental contribution within a factor equals 1

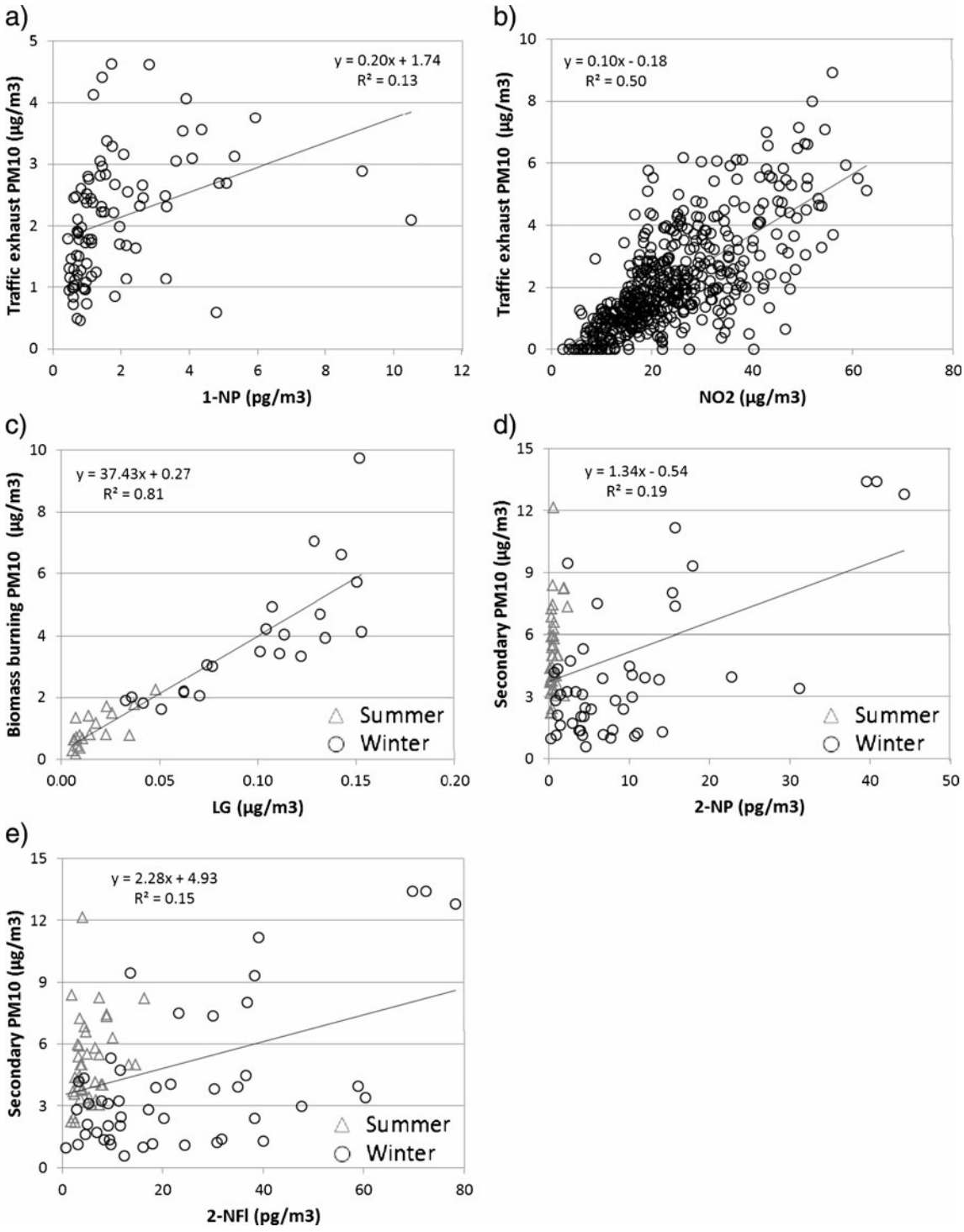


Fig. 5 Comparison of source contributions with biomarkers: traffic exhaust PM_{10} versus **a** 1-NP and **b** NO_2; **c** biomass burning PM_{10} versus levoglucosan; secondary particles versus **d** 2-NP and **e** 2-NFl. The individual regression equations correspond to all data combined

The seasonal differences with higher concentrations in winter than summer (Fig. 3b) were not related to traffic counts, which were higher in summer (Ducret-Stich et al. 2013) but rather to the meteorology. Air pollution levels were generally higher in winter than in summer due to lower wind speeds and lower mixing heights including frequent inversions in this valley (Ducret-Stich et al. 2013). In Fig. 6, exhaust and non-exhaust (i.e., resuspended road dust, tire, and brake wear) traffic source contributions were compared between sites at different distances from the highway. For traffic exhaust, a clear gradient was observed with the higher contributions being closer to the highway.

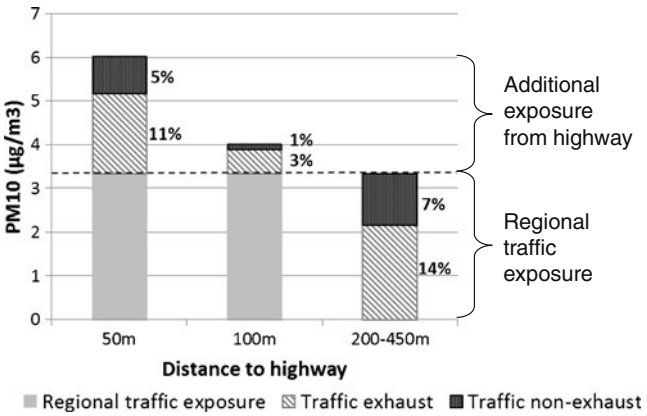


Fig. 6 Spatial distribution of traffic source contributions for the year 2008. Concentrations are normalized by the ratio of the concurrently measured PM_{10} and the annual average PM_{10} measured at the highway site. Data were averaged as follows: site 1 (50 m), site 2 (100 m), average of sites 4–6 (200–450 m). Exclusions: site 3 (only nine samples) and site 7 (protected by tunnel and noise wall)

Some recent studies have used EC and OC fractions to apportion traffic exhaust into diesel and gasoline sources (Kim and Hopke 2005; Kim and Hopke 2004; Liu et al. 2006). However, in our attempt to use EC and OC fractions in the PMF analysis, the traffic exhaust factor was not split. It must be mentioned that for the analysis with fractions, only two thirds of the data were available due to different procedures in the analysis of EC and OC (see "Chemical analysis").

Road dust

Road dust profiles are often difficult to identify due to similar elements seen in mineral dust. Our road dust profile included Si and Fe but differed from mineral dust with a high contribution of Ca (Hueglin et al. 2005; Schauer et al. 2006; Thorpe and Harrison 2008) (Fig. 3a). Contributions of this factor were higher in spring and summer (Fig. 3b), probably due to dryer weather conditions enhancing resuspension. They were also higher on weekdays, probably due to the heavy duty traffic (Online Resource Fig. S4c), which causes more resuspension of road dust than passenger cars (Bukowiecki et al. 2010; Gehrig et al. 2004).

Tire and brake wear

Tire and brake wear contributed to higher concentrations of Cu, Fe, Zn, and Pb (Bukowiecki et al. 2010; Schauer et al. 2006; Thorpe and Harrison 2008) (Fig. 3a). Concentration levels were a little elevated in winter (Fig. 3b) probably caused by higher abrasion of winter tires and increased braking due to the weather conditions. Higher concentrations were again observed on weekdays (Online Resource Fig. S4d) likely the result of heavy duty truck traffic (Bukowiecki et al. 2010).

Road salt

The de-icing road salt factor had a very clear signature with more than 80 % of Na and Cl apportioned to it (Gianini et al. 2012a) (Fig. 3a). This factor was only seen in winter (Fig. 3b) and showed no differences with respect to day of the week.

Biomass

The biomass burning profile was characterized by high concentrations of K, EC, and OC (Gianini et al. 2012b; Khalil and Rasmussen 2003; Reid et al. 2005) and other typical elements for wood smoke (Rb, S, Fe, Ca) (Godoy et al. 2005; Reid et al. 2005) (Fig. 4a). The EC/OC ratio was 0.24, which was on the upper level compared with other studies in Switzerland (Gianini et al. 2012b; Szidat et al. 2006). This somewhat higher ratio might be explained by higher contributions from EC combined with substantial amounts of Pb and Zn observed in the profile (Fig. 4a) pointing to a mixture of biomass burning with some traffic. This was supported by factor contributions in summer, when almost no biomass burning should have been present (Fig. 4b). Nevertheless, PM_{10} contribution from this biomass profile was highly correlated with the known wood biomarker levoglucosan (R^2=0.81, Fig. 5c). In winter, OC also showed a good correlation with biomass burning (R^2=0.72), whereas EC primarily originated from traffic (R^2=0.86) (Online Resource Fig. S5).

Secondary particles

The secondary particle factor included about 75 % of MM, 50 % of S, and about 30 % of OC (Fig. 4a). MM was assumed to represent nitrates and part of the organic matter (see "Mass closure") while S associated with OC represented sulfates in the secondary aerosol (Gianini et al. 2012a; Kim et al. 2003a). Except during two inversion episodes in December 2007 and January 2009, this factor showed generally higher contributions in spring and summer (Fig. 4b), when increased photochemical activity is favoring the formation of secondary particles (Kim et al. 2003a; Seinfeld and Pandis 2006). This result was also shown by the measured ratio between 2-nitrofluoranthene and 2-nitropyrene (2-NFl/2-NP) of 5.7 (9.0 in summer, 2.6 in winter) indicating that secondary particles were mainly formed by reaction with daytime OH– rather than NO_3-radicals (Arey et al. 1986). Nevertheless, the correlations between secondary PM_{10} and 2-NFl or 2-NP were small with an R^2 of 0.15 and 0.19, respectively (Fig. 5d, e). These results were heavily influenced by the very low concentrations of 2-NFl and 2-NP in summer showing almost no correlation with secondary PM_{10}. Correlations in winter were stronger with 0.40 and 0.49 for 2-NFl and 2-NP, respectively. In contrast to daily secondary particle contributions, nitro-PAHs were

only available as weekly concentrations leading to generally low correlations. Also, some of the nitro-PAHs may be present as a result of sampling artifacts (Schauer et al. 2003) and thereby lower the observed correlations.

Mineral factors

Contributions from mineral sources were split into two profiles: mineral dust and construction site emissions (railway tunnel "Alp Transit") (Fig. 4a). The crustal elements Si, Al, Ca, and Fe were shared by both profiles. While most of the Si was apportioned to mineral dust, almost all Mg was present in the construction site factor. Mg as an additive to the concrete, which was prepared with recycled excavated material and used on site, might have caused the PMF to apportion Mg unevenly between the two sources. The construction site factor also contained substantial amounts of Ca and Zn. These elements might be explained by the extensive use of lubricating oil for drilling machines in the tunnel as well as conveyor belts and diesel locomotives outside. Ratios of Ca/Al, K/Al, and Fe/Al for the mineral dust factor (0.64, 1.03, and 2.02, respectively) and for the construction site factor (1.80, 0.0, and 0.85, respectively) were different compared with the geogenic ratios (1.15, 0.61, and 1.13, respectively) in northern Switzerland (Gianini et al. 2012b). However, the ratios of the two source profiles combined were again similar to the geogenic ratios with Ca/Al=1.14, K/Al=0.59, and Fe/Al=1.52. PMF was not able to clearly split these two sources, which was also reflected in the persistently observed correlations in the *G space* plots between these two factors. If additional information were available on the composition of the material from either source, then a clearer separation such as that obtained by Amato et al. (2009) might have been possible. Both mineral factors showed similar weekday patterns with peaks on Tuesdays and Thursdays (Online Resource Fig. S4e). These peaks might be driven by some activity patterns on the construction site, because all high mineral factor concentrations were measured at site 5, which was closest to the construction site. Due to the similarities of the two factors, we combined them to one total mineral dust factor for the description of contributions in "Source contributions."

Railway

The railway profile showed typical abrasion elements such as Fe, Cu, manganese (Mn), chromium (Cr), and nickel (Ni) (Bukowiecki et al. 2007) (Fig. 4a). However, Cu, Mn, and

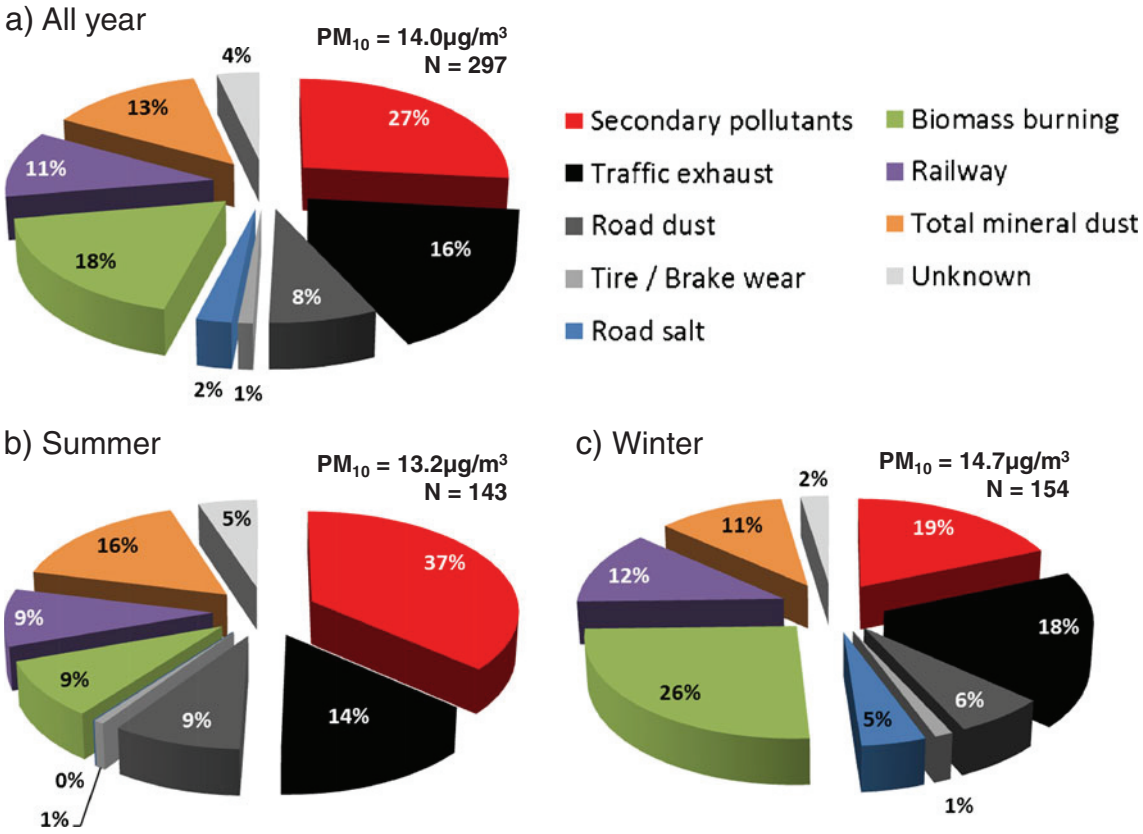


Fig. 7 Average source contributions for the year 2008: **a** the whole year, **b** in summer (Apr–Sep), and **c** in winter (Oct–Mar). Average daily PM_{10} concentrations with number of measurements for the respective measurement periods are shown adjacent to the pie charts

Cr were emitted in very low quantities compared with Fe (Cu/Fe=0.01, Mn/Fe=0.01, Cr/Fe<0.005) comparable to a study in Zürich (Gehrig et al. 2007). In Switzerland, trains nearly exclusively operate with electric locomotives. However, due to the absence of power lines, diesel locomotives were used for the construction site. This presence of diesel engines might explain the additional contributions of Ba, Zn, EC, and OC in the source profile (Fig. 4a). Contributions of this factor were always highest at the site 5, which was closest to the railway tracks (Fig. 8).

Source contributions

In Fig. 7, source contributions are summarized by season for all sites in Erstfeld. To prevent over-representation of the winter months, only data from the year 2008 were used. To compare the contributions among the sites and seasons (Fig. 8), the sites closest to the highway (sites 1-3, Fig. 1) were excluded because of limited and unbalanced data in 2008 for these sites (i.e., only summer data for site 1 (N=9), only winter data for site 2 (N=32) and site 3 (N=9)). Overall, secondary pollution was the main contributor to PM_{10} in summer, while traffic and biomass burning were more important in winter (Fig. 7). In summer, greater photochemical activity boosts the formation of secondary pollutants, while stable air masses and frequent inversions trap the pollutants in the valley in winter, increasing the importance of local sources such as traffic and biomass burning. The importance of secondary pollution in Erstfeld was also reflected in the ratio of 2-nitrofluoranthene and 1-nitropyrene (2-NFl/1-NP), which was >5 at all sites except site 1, indicating a domination of nitro-PAHs by atmospheric reactions rather than primary emissions (Miller-Schulze et al. 2010).

Although total PM_{10} concentrations were spatially homogeneously distributed (Ducret-Stich et al. 2013), large differences were observed for local traffic, railway, and mineral contributions to PM_{10} (Fig. 8). In both seasons, relative traffic source contributions were higher close to the highway (Figs. 6 and 8). At site 5, which was only 22 m away from the railway tracks and the closest measuring station to the construction site, we observed the highest contribution from the railway and mineral sources (Fig. 8).

The average PM_{10} concentration of 14.0 μg/m^3 in this study was lower compared with other sites from the Swiss national air pollution monitoring network (NABEL) (Gianini

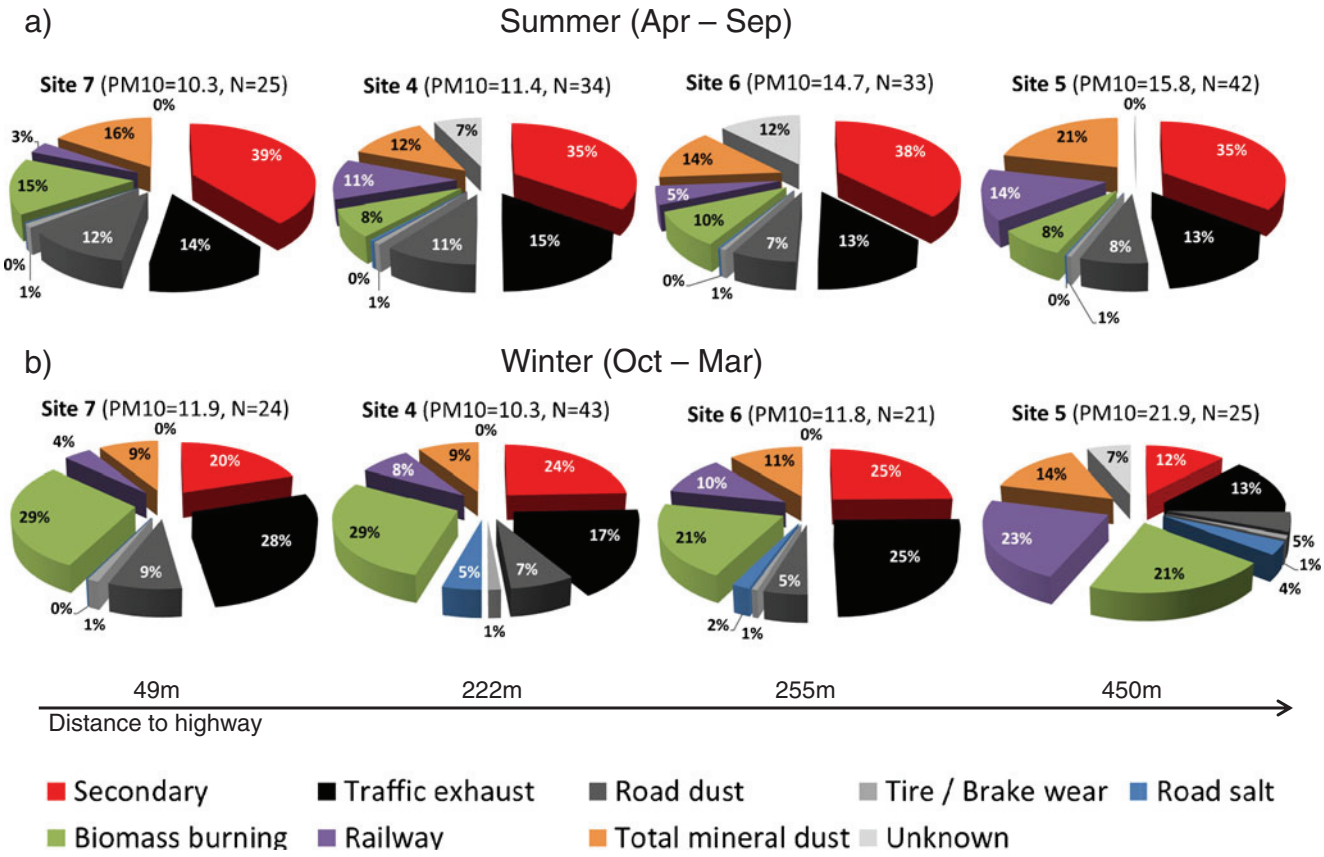


Fig. 8 Estimated source contributions by season for the four sites in the residential area for the year 2008. Site 7 is protected by a tunnel and a noise barrier from the direct influence of the highway; site 5 is closest to the railway and the construction site. Average daily PM_{10} concentrations [micrograms per cubic meter] together with number of measurements at various sites are presented in *brackets*

et al. 2012b) and comparable to other European rural background sites (Putaud et al. 2010). However, the relative contribution to PM_{10} of total traffic (i.e., exhaust, road dust, tire and brake wear) was about 25 %, which was higher than in Zürich (18 %, urban background), almost as high as in Bern (30 %; urban roadside), and comparable to the rural site Magadino (24 %) south of the Alps, which is also influenced by the same highway as in our study (Gianini et al. 2012a). These results emphasize the large influence of highway traffic on the composition of particulate matter.

Secondary pollution contributions (27 %) were again comparable to Magadino (29 %) and lower than at all other NABEL sites (37–52 %) (Gianini et al. 2012a). In the European context, secondary aerosol contributions were comparable to urban sites in Central Europe (Putaud et al. 2010). This lower contribution might be a result of less photochemical activity due to the decreased sunlight in the narrow mountain valley of Erstfeld. Also, PMF might underestimate the contribution of this factor due to the lack of measurements of sulfate, nitrate, and ammonium in this study.

Another important source was biomass burning (primarily wood burning in winter). With a relative contribution of 18 %, biomass PM_{10} was higher in our study than at NABEL sites (11–14 %), except for Magadino, which had a very high contribution of 31 % (Gianini et al. 2012a). In other studies, close to Magadino, it has been shown that wood burning is a major source in this region (Sandradewi et al. 2008; Szidat et al. 2007). The combination of the mountain–valley terrain, strong inversion conditions in winter, and extensive use of wood as a home heating fuel led to these high contributions to PM_{10}.

In Erstfeld, the construction site was probably the reason for the higher total mineral dust (i.e., mineral dust and construction site) contribution of 13 % compared with other rural sites in Central Europe (9 %) (Putaud et al. 2010) and the NABEL sites in Switzerland (8–13 %) (Gianini et al. 2012a).

As the result of having an extensive data set of daily measurements from seven different monitoring sites within the valley over one and a half years, we were able to separate different sources spatially and seasonally even though our study region was rather small. Also, additionally measured biomarkers (i.e., levoglucosan, NPAHs) allowed us to independently compare and validate some of the source contributions. However, as measurements were not concurrently collected at the different sites and no representative background measurements were available, it was not possible to compare daily contributions between the sites. The aim to distinguish between diesel and gasoline traffic sources from the highway could also not be achieved. Because of the method change in the EC and OC analysis, comparable fractionated data were only available for part of the data set. Using only the subsets, PMF was not able to give stable results.

Conclusions

In general, traffic, secondary particles from precursors of various sources—including traffic—and biomass burning were the major contributors to PM_{10} in the alpine village of Erstfeld in 2008 accounting for 27 %, 27 %, and 18 % of the total PM_{10} concentrations, respectively. PM_{10} exposure attributed to traffic was more comparable to urban sites than those observed in rural sites in Switzerland. Also, a clear spatial dependency from the nearby highway was observed, showing increasing contributions of traffic exhaust and non-exhaust PM_{10} with decreasing distance to the highway. While secondary particle contributions were lower, the biomass burning contributions were higher in Erstfeld compared with other northern Swiss villages, due to the combination of topography, winter inversions, and the importance of wood as an energy source in the Alps. However, contributions were much lower than in Magadino in the southern Alps, where biomass burning is known to be the major source of PM. The local influences of railway traffic and a major construction site were also observed. These receptor modeling results are being used to investigate the source-specific impact of air pollution exposures on short-term respiratory health outcomes in children in the village.

Acknowledgments This work was funded by the Federal Office for the Environment FOEN (No. 050303 / G161-1955) of the Swiss Government. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the FOEN. The authors declare they have no competing financial interests. We would like to thank Peter Boehler and Raffael Kaenzig from inNET Monitoring AG (Altdorf, Switzerland) for conducting the extensive air pollution measurements. We are also grateful to Christoph Hüglin and Matthias Gianini at Empa (Dübendorf, Switzerland) and to Chang-Fu Wu at National Taiwan University for their helpful inputs to the PMF analysis.

References

Albinet A, Leoz-Garziandia E, Budzinski H, Villenave E (2007) Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): concentrations and sources. Sci Total Environ 384:280–292. doi:10.1016/j.scitotenv.2007.04.028

Amato F, Pandolfi M, Escrig A, Querol X, Alastuey A, Pey J, Perez N, Hopke PK (2009) Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF2. Atmos Environ 43:2770–2780. doi:10.1016/j.atmosenv.2009.02.039

Arey J, Zielinska B, Atkinson R, Winer AM, Ramdahl T (1967) Pitts Jr JN (1986) The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NOx. Atmos Environ 20:2339–2345. doi:10.1016/0004-6981(86)90064-8

Brugge D, Durant J, Rioux C (2007) Near-highway pollutants in motor vehicle exhaust: a review of epidemiologic evidence of cardiac and pulmonary health risks. Environ Health 6:23. doi:10.1186/1476-069X-6-23

Bukowiecki N, Gehrig R, Hill M, Lienemann P, Zwicky CN, Buchmann B, Weingartner E, Baltensperger U (2007) Iron, manganese and copper emitted by cargo and passenger trains in Zürich (Switzerland): size-segregated mass concentrations in ambient air. Atmos Environ 41:878–889. doi:10.1016/j.atmosenv.2006.07.045

Bukowiecki N, Lienemann P, Hill M, Furger M, Richard A, Amato F, Prévôt ASH, Baltensperger U, Buchmann B, Gehrig R (2010) PM10 emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland. Atmos Environ 44:2330–2340. doi:10.1016/j.atmosenv.2010.03.039

Chow JC, Watson JG, Fujita EM, Lu Z, Lawson DR, Ashbaugh LL (1994) Temporal and spatial variations of PM2.5 and PM10 aerosol in the Southern California air quality study. Atmos Environ 28:2061–2080. doi:10.1016/1352-2310(94)90474-X

Davidson CI, Phalen RF, Solomon PA (2005) Airborne particulate matter and human health: a review. Aerosol Sci Tech 39:737–749. doi:10.1080/02786820500191348

Ducret-Stich RE, Tsai MY, Ragettli MS, Ineichen A, Kuenzli N, Phuleria HC (2013) Role of highway traffic on spatial and temporal distributions of air pollutants in a Swiss Alpine valley. Sci Total Environ. doi:10.1016/j.scitotenv.2013.03.065

e-CFR: Title 40: Protection of environment; part 136-guidelines establishing test procedures for the analysis of pollutants [WWW Document] (2012). URL http://www.ecfr.gov/cgi-bin/text-idx?c=ecfr&SID=4310ba4cbc37140550f957fc4aab5841&rgn=div5&view=text&node=40:24.0.1.1.1&idno=40#40:24.0.1.1.1.0.1.8.2

Gehrig R, Hill M, Imhof D, Weingartner E, Baltensperger U (2004) Separate determination of PM10 emission factors of road traffic for tailpipe emissions and emissions from abrasion and resuspension processes. Int J Environ Pollut 22:312–325

Gehrig R, Hill M, Lienemann P, Zwicky CN, Bukowiecki N, Weingartner E, Baltensperger U, Buchmann B (2007) Contribution of railway traffic to local PM10 concentrations in Switzerland. Atmos Environ 41:923–933. doi:10.1016/j.atmosenv.2006.09.021

Gianini MFD, Fischer A, Gehrig R, Ulrich A, Wichser A, Piot C, Besombes J-L, Hueglin C (2012a) Comparative source apportionment of PM10 in Switzerland for 2008/2009 and 1998/1999 by positive matrix factorisation. Atmos Environ 54:149–158. doi:10.1016/j.atmosenv.2012.02.036

Gianini MFD, Gehrig R, Fischer A, Ulrich A, Wichser A, Hueglin C (2012b) Chemical composition of PM10 in Switzerland: an analysis for 2008/2009 and changes since 1998/1999. Atmos Environ 54:97–106. doi:10.1016/j.atmosenv.2012.02.037

Godoy MLDP, Godoy JM, Artaxo P (2005) Aerosol source apportionment around a large coal fired power plant—thermoelectric complex Jorge Lacerda, Santa Catarina, Brazil. Atmos Environ 39:5307–5324. doi:10.1016/j.atmosenv.2005.05.033

Hazenkamp-von Arx MH, Schindler C, Ragettli M, Künzli N, Braun-Fahrländer C, Liu L-J (2011) Impacts of highway traffic exhaust in alpine valleys on the respiratory health in adults: a cross-sectional study. Environ Health 10:13. doi:10.1186/1476-069X-10-13

Health Effects Institute (2010) HEI panel on the health effects of traffic-related air pollution. Traffic-related air pollution: a critical review of the literature on emissions, exposure, and health effects. Health Effects Institute, Boston

Hopke PK (2003) Recent developments in receptor modeling. J Chemometr 17:255–265. doi:10.1002/cem.796

Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H (2005) Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. Atmos Environ 39:637–651. doi:10.1016/j.atmosenv.2004.10.027

Jordan TB, Seen AJ, Jacobsen GE (2006) Levoglucosan as an atmospheric tracer for woodsmoke. Atmos Environ 40:5316–5321. doi:10.1016/j.atmosenv.2006.03.023

Karanasiou A, Moreno N, Moreno T, Viana M, De Leeuw F, Querol X (2012) Health effects from Sahara dust episodes in Europe: literature review and research gaps. Environ Int 47:107–114. doi:10.1016/j.envint.2012.06.012

Khalil MA, Rasmussen R (2003) Tracers of wood smoke. Atmos Environ 37:1211–1222. doi:10.1016/S1352-2310(02)01014-2

Kim E, Hopke PK (2005) Improving source apportionment of fine particles in the Eastern United States utilizing temperature-resolved carbon fractions. J Air Waste Manag 55:1456–1463. doi:10.1080/10473289.2005.10464748

Kim E, Hopke PK (2004) Source apportionment of fine particles in Washington, DC, utilizing temperature-resolved carbon fractions. J Air Waste Manag 54:773–785. doi:10.1080/10473289.2004.10470948

Kim E, Hopke PK, Edgerton ES (2003a) Source identification of Atlanta aerosol by positive matrix factorization. J Air Waste Manag 53:731–739. doi:10.1080/10473289.2003.10466209

Kim E, Hopke PK, Paatero P, Edgerton ES (2003b) Incorporation of parametric factors into multilinear receptor model studies of Atlanta aerosol. Atmos Environ 37:5009–5021. doi:10.1016/j.atmosenv.2003.08.035

Laumbach RJ, Kipen HM (2012) Respiratory health effects of air pollution: update on biomass smoke and traffic pollution. J Allergy Clin Immun 129:3–11. doi:10.1016/j.jaci.2011.11.021

Liu W, Wang Y, Russell A, Edgerton ES (2006) Enhanced source identification of southeast aerosols using temperature-resolved carbon fractions and gas phase components. Atmos Environ 40(2):445–466. doi:10.1016/j.atmosenv.2005.11.079

Lough GC, Christensen CG, Schauer JJ, Tortorelli J, Mani E, Lawson DR, Clark NN, Gabele PA (2007) Development of molecular marker source profiles for emissions from on-road gasoline and diesel vehicle fleets. J Air Waste Manag 57:1190–1199. doi:10.3155/1047-3289.57.10.1190

Miller-Schulze JP, Paulsen M, Toriba A, Tang N, Hayakawa K, Tamura K, Dong L, Zhang X, Simpson CD (2010) Exposures to particulate air pollution and nitro-polycyclic aromatic hydrocarbons among taxi drivers in Shenyang, China. Environ Sci Technol 44:216–221. doi:10.1021/es802392u

Naeher LP, Brauer M, Lipsett M, Zelikoff JT, Simpson CD, Koenig JQ, Smith KR (2007) Woodsmoke health effects: a review. Inhal Toxicol 19:67–106. doi:10.1080/08958370600985875

Norris G, Vedantham R, Wade K, Brown S, Prouty J, Foley C (2008) EPA positive matrix factorization (PMF) 3.0 fundamentals & user guide. Washington DC, USA

Paatero P (1997) Least squares formulation of robust non-negative factor analysis. Chemometr Intell Lab 37:23–35. doi:10.1016/S0169-7439(96)00044-5

Paatero P, Hopke PK (2003) Discarding or downweighting high-noise variables in factor analytic models. Anal Chim Acta 490:277–289. doi:10.1016/S0003-2670(02)01643-4

Paatero P, Hopke PK, Begum BA, Biswas SK (2005) A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution. Atmos Environ 39:193–201. doi:10.1016/j.atmosenv.2004.08.018

Paatero P, Hopke PK, Song X-H, Ramadan Z (2002) Understanding and controlling rotations in factor analytic models. Chemometr Intell Lab 60:253–264. doi:10.1016/S0169-7439(01)00200-3

Paatero P, Tapper U (1994) Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5:111–126. doi:10.1002/env.3170050203

Polissar AV, Hopke PK, Paatero P, Malm WC, Sisler JF (1998) Atmospheric aerosol over Alaska: 2. Elemental composition and sources. J Geophys Res 103:19045–19,057. doi:10.1029/98JD01212

Pope CA, Dockery DW (2006) Health effects of fine particulate air pollution: lines that connect. J Air Waste Manag 56:709–742. doi:10.1080/10473289.2006.10464485

Putaud J-P, Van Dingenen R, Alastuey A, Bauer H, Birmili W, Cyrys J et al (2010) A European aerosol phenomenology—3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos Environ 44:1308–1320. doi:10.1016/j.atmosenv.2009.12.011

Reid JS, Koppmann R, Eck TF, Eleuterio DP (2005) A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. Atmos Chem Phys 5:799–825

Ringuet J, Albinet A, Leoz-Garziandia E, Budzinski H, Villenave E (2012a) Reactivity of polycyclic aromatic compounds (PAHs, NPAHs and OPAHs) adsorbed on natural aerosol particles exposed to atmospheric oxidants. Atmos Environ 61:15–22. doi:10.1016/j.atmosenv.2012.07.025

Ringuet J, Leoz-Garziandia E, Budzinski H, Villenave E, Albinet A (2012b) Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France). Atmos Chem Phys 12:8877–8887. doi:10.5194/acp-12-8877-2012

Russell AG, Brunekreef B (2009) A focus on particulate matter and health. Environ Sci Technol 43:4620–4625. doi:10.1021/es9005459

Sandradewi J, Prévôt ASH, Szidat S, Perron N, Alfarra MR, Lanz VA, Weingartner E, Baltensperger U (2008) Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. Environ Sci Technol 42:3316–3323. doi:10.1021/es702253m

Schauer C, Niessner R, Pöschl U (2003) Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts. Environ Sci Technol 37:2861–2868

Schauer JJ, Lough GC, Shafer MM, Christensen WF, Arndt MF, DeMinter JT, Park JS (2006) Characterization of metals emitted from motor vehicles. Res Rep Health Eff Inst 1–76; discussion 77–88

Scheepers PTJ, Martens MHJ, Velders DD, Fijneman P, Van Kerkhoven M, Noordhoek J, Bos RP (1995) 1-Nitropyrene as a marker for the mutagenicity of diesel exhaust-derived particulate matter in workplace atmospheres. Environ Mol Mutagen 25:134–147. doi:10.1002/em.2850250207

Seinfeld JH, Pandis SN (2006) Atmos Chem Phys: from air pollution to climate change. John Wiley & Sons, New York, NY

Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MP, Rogge WF, Cass GR (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos Environ 33:173–182. doi:10.1016/S1352-2310(98)00145-9

Simpson CD, Dills RL, Katz BS, Kalman DA (2004) Determination of levoglucosan in atmospheric fine particulate matter. J Air Waste Manag 54:689–694. doi:10.1080/10473289.2004.10470945

Stanek LW, Sacks JD, Dutton SJ, Dubois J-JB (2011) Attributing health effects to apportioned components and sources of particulate matter: an evaluation of collective results. Atmos Environ 45:5655–5663. doi:10.1016/j.atmosenv.2011.07.023

Sweetman JA, Zielinska B, Atkinson R, Ramdahl T, Winer AM (1967) Pitts Jr. JN (1986) A possible formation pathway for the 2-nitrofluoranthene observed in ambient particulate organic matter. Atmos Environ 20:235–238. doi:10.1016/0004-6981(86)90230-1

Szidat S, Jenk TM, Synal H-A, Kalberer M, Wacker L, Hajdas I, Kasper-Giebl A, Baltensperger U (2006) Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14C. J Geophys Res 111, D07206. doi:10.1029/2005JD006590

Szidat S, Prévôt ASH, Sandradewi J, Alfarra MR, Synal H-A, Wacker L, Baltensperger U (2007) Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophys Res Lett 34, L05820. doi:10.1029/2006GL028325

Thorpe A, Harrison RM (2008) Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci Total Environ 400:270–282. doi:10.1016/j.scitotenv.2008.06.007

Turpin BJ, Lim H-J (2001) Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci Tech 35:602–610. doi:10.1080/02786820119445

US EPA (2009) Integrated science assessment for particulate matter (final report). U.S. Environmental Protection Agency, Washington DC, USA

Viana M, Kuhlbusch TAJ, Querol X, Alastuey A, Harrison RM, Hopke PK et al (2008) Source apportionment of particulate matter in Europe: a review of methods and results. J Aerosol Sci 39:827–849. doi:10.1016/j.jaerosci.2008.05.007

Wu C, Larson TV, Wu S, Williamson J, Westberg HH, Liu L-JS (2007) Source apportionment of PM2.5 and selected hazardous air pollutants in Seattle. Sci Total Environ 386:42–52. doi:10.1016/j.scitotenv.2007.07.042

4. Traffic-related short-term health effects in children with asthma

Results of this chapter are subject of a future publication

4.1. Background

Ambient air pollution has previously been reported as a major risk factor for cardio-respiratory diseases (Perez et al., 2010; Kelly and Fussell, 2011), especially traffic-related air pollution (Brugge et al., 2007). Children are particularly susceptible to the effects of air pollution exposure as their lungs are still in development (Gauderman et al., 2007), and there is vast evidence of short-term air pollution effects on respiratory symptoms in children with asthma (Weinmayr et al., 2010). An increasing number of studies are also investigating the impact of traffic-related air pollution on inflammatory markers such as fractional exhaled nitric oxide (FeNO), and on oxidative stress markers in exhaled breath condensate (eBC) (Laumbach and Kipen, 2010).

Within the framework of MfM-U (Monitoring flankierende Massnahmen – Umwelt), two cross-sectional questionnaire studies on respiratory symptoms were conducted with adults (Hazenkamp-von Arx et al., 2011) and with children (Ragettli, 2009) living along a Swiss alpine highway corridor in 2005 and 2007/08, respectively. Hazenkamp-von Arx *et al.* (2011) found increased covariate-adjusted odds of reporting wheezing and chronic cough (odds ratio (OR) between 2.4 and 3.1) for adults living within 200 meter of a highway. In the children study, residential traffic exposure was modeled using the PolluMap dispersion model (FOEN, 2003, 2004). This allowed predictions of source-specific annual average exposures to PM_{10}, $PM_{2.5}$, and NO_x from passenger and freight traffic at subjects' home locations. Reports of wheezing, hay fever, and asthma symptoms were increased by 15-30% per inter quartile range (IQR) increment of PM_{10} or $PM_{2.5}$ from both, passenger and freight traffic. The same albeit non-significant trends were observed for NO_2. These studies provide evidence that residential exposure to highway traffic increases respiratory symptoms in rural regions with no other major local air pollution sources. However, the above studies used a cross-

sectional design with subjectively measured health outcomes. In addition, exposure was approximated by distance to highway or annual dispersion model estimates. To improve the health and air pollution exposure assessment, a panel study was funded to investigate the short-term effects of local traffic-related air pollution on the course of asthma in children living in Erstfeld by more objective health outcomes and extensive air pollution monitoring at children's homes.

4.2. Methods

From November 2007 to June 2009, thirteen children (ages 7-13) with doctor-diagnosed asthma living in Erstfeld participated in monthly monitoring of respiratory health indicators including inflammatory markers (fractional exhaled nitric oxide FeNO) and oxidative stress markers (nitrite, pH, hydrogen peroxide (H_2O_2), cytokines) in exhaled breath condensate. Monthly visits took place at the local primary school between 12:00 and 13:30. Children were asked to forgo food intake for one hour before health measurements. At each visit, they had to complete questionnaires on asthma symptoms, health status, inhaler and medication use, exposure to smoking, home ventilation and a time activity diary for the prior 24 hours. A baseline questionnaire about age, sex, socioeconomic status, birth history, health history, home characteristics, living environment and pets was completed by the parents. Allergy status of the children was determined by skin prick test for 22 different allergens (pollen, animals, molds, dust mites).

Measurement of fractional exhaled nitric oxide (FeNO)

At each monthly visit, three offline FeNO measurements were taken per child by flow controlled (constant pressure between 10-15cm H_2O) collection of exhaled breath in Mylar balloons (Figure 4–1) followed by NO analysis within two to three hours after collection with a Sievers Chemiluminescence NO Analyser (Koenig et al., 2003).

Figure 4–1: Offline collection of FeNO.

The median values of the three samples per child were used for the health analysis. In addition, three ambient air samples were collected during each sampling session at the primary school.

Collection and analysis of exhaled breath condensate (eBC)

Exhaled breath condensate was collected during tidal breathing for ten minutes through an RTube (Respiratory Research, Inc., Charlottesville, VA, USA) covered by a cooling sleeve following manufacturer guidelines (Figure 4–2). Samples were transported on dry ice and stored in the freezer (-80 C) until analysis. Aliquots of the thawed samples were used for the different analyses of biomarkers:

Figure 4–2: Collection of exhaled breath condensate

pH: Breath condensate samples were de-aerated with argon gas before pH was measured with a micro electrode pH meter (Horvath et al., 2005).

Nitrite: Nitrite concentration in the breath condensate was determined on triplet samples by a Griess reaction assay (Ho et al., 1998). Median values of each triplet were used for the health analysis.

H_2O_2: Hydrogen peroxide was analyzed using an Amplex Red H2O2 Assay Kit. This analysis was done only once. Only 50% of the samples had H_2O_2 levels above the detection limit and they showed a strong correlation with the storage time. Therefore we did not use this data for any analysis.

Cytokines: We used a Bio-Plex 200 system Cytokine Assay (Bio Rad, Hercules, CA, USA) to measure levels of different cytokines (IL-4, IL-5, IL-8, IL-13, and GM-CSF) in the breath condensate samples. As reported in other studies (Rosias et al., 2004; Bayley et al., 2008), most of our cytokine levels were also below detection limit: 100% for IL-5, 83% for IL-8, and 95% for IL-4, IL-13 and GM-CSF. Therefore we could not use any cytokines in our health analysis.

Exposure

An extensive air pollution monitoring was done for the whole study period. This is described in detail in Article 2. In short, two fixed (background and highway) and seven mobile sites were monitored for daily PM_{10}, EC, OC, as well as continuous particle number concentrations and NO_x. In addition, 14-day integrated NO_2 concentrations were measured with passive samplers outdoors and indoors of the participants homes prior to the health monitoring. A land-use regression model was built to estimate home outdoor concentrations of NO_2 (Article 2), and source contributions to PM_{10} were estimated by Positive Matrix Factorisation (PMF) (Article 3).

Statistical analysis

Because our interest was in the changes of the health marker levels within children, we applied mixed linear models for repeated measurements within subjects using an autoregressive covariate structure (AR(1)) in SAS 9.2 (SAS Institute, Cary, NC,USA). As distributions of FeNO and eBC nitrite were highly skewed, we used log-transformed data for the analysis. For each outcome variable (*i.e.* log FeNO, log nitrite, pH), we build a base model by backward selection with a significance level of p=0.2 for retention. The following variables have been considered: log FeNO, log nitrite, pH, log ambient NO, age, gender, asthma symptoms on same or previous day, use of inhaler on same or previous day, presence of cold or flu, allergy symptoms in the previous month, exposure to environmental tobacco smoke (ETS) in the previous 24 hours, ambient temperature and temperature squared, relative humidity, and sine and cosine functions of day of the year.

In the second step, we assessed the relationship between the health outcomes and the different pollutants (*i.e.* NO_2 estimates from the home outdoor model, total PM_{10} and EC measured at the highway and source-specific PM_{10}) by adding them to the core models. Different time windows of the pollutants were analyzed: the day before the health measurement (lag1), the average of the two prior days (lag1, 2), and the average of the three prior days (lag1-3). Each model also included ozone because of previously reported associations with biomarkers (Barraza-Villarreal et al., 2008). Interactions between core model and air pollution

variables were also investigated. Effect estimates for air pollutants were scaled per interquartile range (IQR). FeNO and eBC nitrite resulting effect estimates (β) were transformed into percent changes using the formula: $(e^{(\beta)}-1)*100$.

4.3. Results

In total we collected 215 individual health measurements in eight girls and five boys. At each visit, the children had to answer questions about symptoms, medication use and special exposure. Variables relevant for the health analysis are summarized in Table 4-1. Inhaler use was much higher than reported asthma symptoms, because some children used it also for prevention. Both, measured health markers and air pollutants were highly variable (Table 4-2). Average concentrations of PM_{10}, EC and NO_2 at the time of the health measurements were slightly higher than the mean values over the whole study of 16.9µg/m^3, 1.65µg/m^3 and 23.1µg/m^3, respectively. The traffic-related pollutants EC, NO_2 and traffic exhaust PM_{10} were highly correlated (Table 4-3). Results for the three biomarkers are described in the following paragraphs.

FeNO

The largest effects of traffic-related air pollutants on FeNO were observed for concentrations on the day before the health measurements (lag1). Therefore we focused on lag1 and lag1,2 air pollution exposure variables in the analysis. In addition, the following variables were included in the models: maximum of 1-hour ozone in the two prior days, allergy symptoms in the previous month, presence of cold or flu, asthma symptoms and use of inhaler on the previous day, gender, day of the week and season. The traffic-related air pollutants NO_2 and EC showed stronger positive associations with FeNO than total and source-specific PM_{10}, although these were not significant (Figure 4–3).

Table 4–1: Summary of variables from monthly questionnaires included in health analysis models.

	yes	no
ETS exposure in prior 24 hours*	30 (14%)	185 (86%)
Allergy symptoms in prior month*	58 (27%)	157 (73%)
Cold or flu*	78 (36%)	137 (64%)
Asthma symptoms on prior day*	8 (4%)	207 (96%)
Use of inhaler on prior day*	69 (32%)	146 (68%)
Asthma symptoms on same day *	2 (1%)	213 (99%)
Use of inhaler on same day*	43 (20%)	172 (80%)

* referring to the time of health monitoring

Table 4–2: Summary of measurements relevant for the health analysis.

	N	Mean (SD)	Min	Max
Health measurements:				
FeNO (ppb)	215	17.04 (14.22)	3.02	75.53
eBC pH	196	7.06 (0.35)	5.88	7.83
eBC nitrite (µM)	179	0.82 (0.54)	0.2	3.57
Exposure measurements:				
Total PM_{10} at highway (µg/m^3) *	215	18.51 (10.17)	4.72	44.72
EC at highway (µg/m^3) *	197	1.76 (0.94)	0.45	4.72
NO_2 from home model (µg/m^3) *	209	24.77 (13.04)	4.62	61.07
PM_{10} traffic exhaust (µg/m^3) *	176	2.66 (1.70)	0.05	6.61
Max. 1-h ozone (µg/m^3)	212	18.35 (11.67)	0.96	44.30
Temperature (°C) *	209	8.38 (7.54)	-3.12	27.07
Ambient NO (ppb)	215	14.61 (24.42)	0.92	121.02

N=Number of measurements; SD=Standard deviation; Min=Minimum; Max=Maximum; * Daily averages.

Table 4–3: Spearman correlation (r) between the different air pollutants.

	Total PM_{10} at highway	EC at highway	NO_2 home model
EC at highway	0.67		
NO2 home model	0.55	0.79	
PM10 Traffic exhaust	0.63	0.82	0.71

Interaction analyses revealed “having a cold” as significant modifier of the effects of total PM_{10}, NO_2 and EC. On days when children reported cold symptoms, there was no change in FeNO levels with increased air pollution concentrations at lag1or lag1,2. However, on days without cold symptoms, increments of the size of one interquartile range in NO_2, EC and total PM_{10} on the prior day were associated with significant increases in FeNO by 15%, 13% and 6%, respectively (Figure 4–4). Another significant interaction was found between allergy symptoms and total PM_{10}. On days following a 30-day period without allergy symptoms increased PM_{10} levels were followed by an average increase in FeNO of 5% (not significant), while no effect on FeNO levels was observed on days following a 30-day period with allergy symptoms.

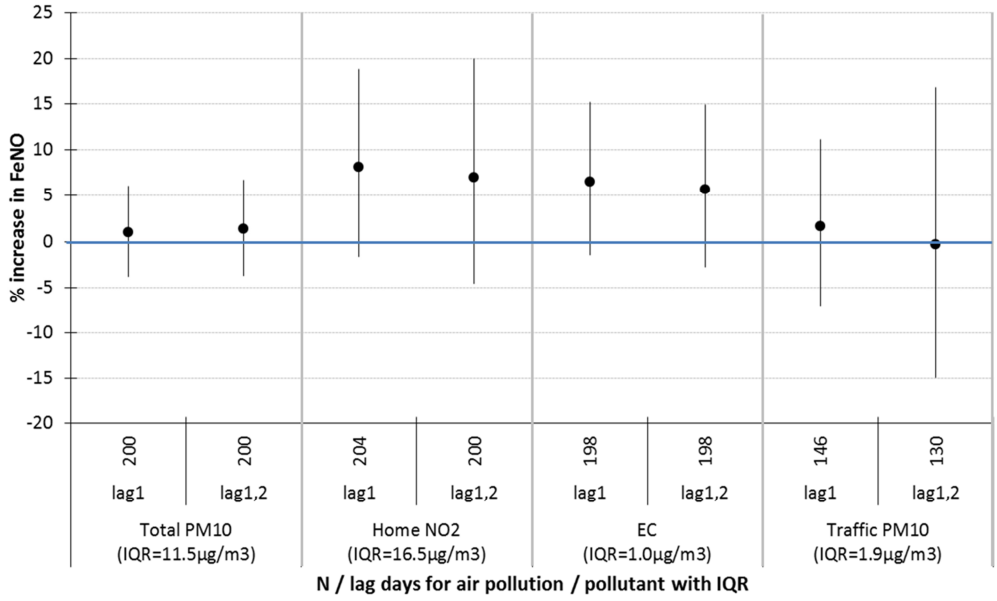


Figure 4–3: Average % increase (with 95% confidence interval) in FeNO if air pollution concentrations at lag1 resp. lag1,2 were increased by the size of one interquartile range (IQR). Models were adjusted for maximum of 1-hour ozone in the two prior days, allergy symptoms in the previous month, presence of cold or flu, asthma symptoms and use of inhaler on the previous day, gender, day of the week and season.

Example: If the concentration of EC was 1µg/m^3 on the day before a first measurement of FeNO and 2µg/m^3 (1µg/m^3 + IQR) on the day before a second measurement, then this second measurement was, on average 6.5% higher than the first FeNO measurement.

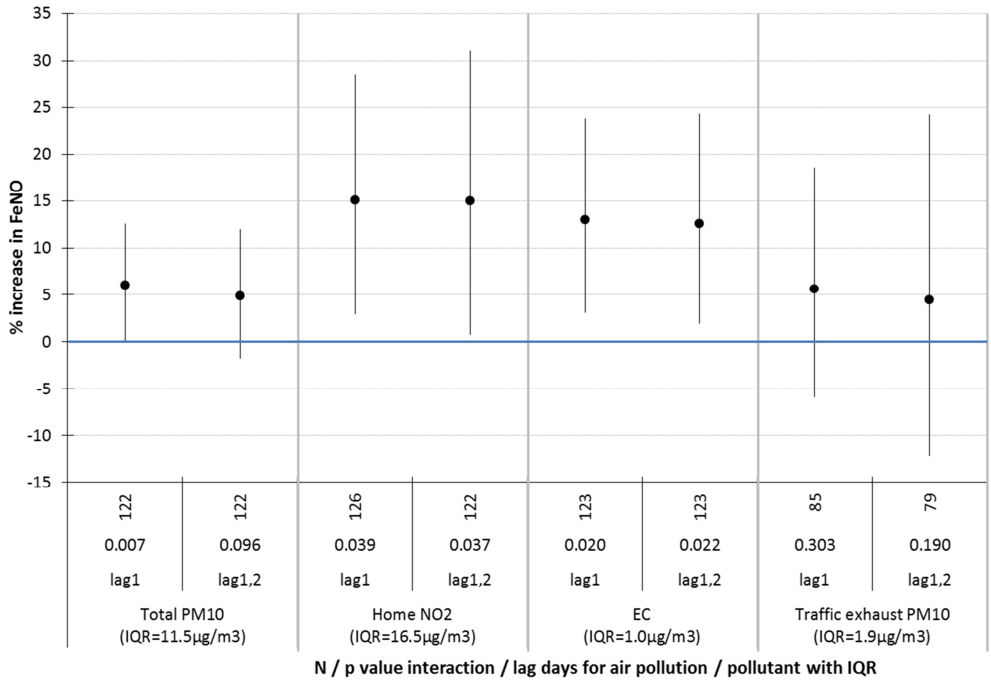


Figure 4–4: Average % increase (with 95% confidence interval) of FeNO on **days without cold symptoms**, if air pollution concentrations at lag1 resp. lag1,2 were increased by the size of one interquartile range (IQR). Models were adjusted for maximum of 1-hour ozone in the two prior days, allergy symptoms in the previous month, asthma symptoms and use of inhaler on the previous day, gender, day of the week and season.

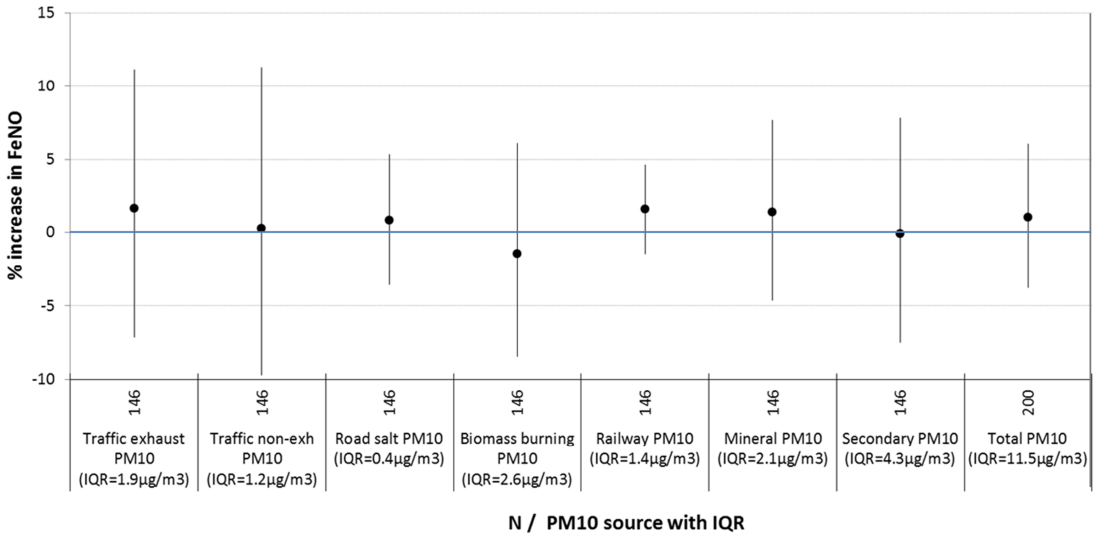


Figure 4–5: Average % increase (with 95% confidence interval) of FeNO if air pollution concentrations at lag1 were increased by the size of one interquartile range (IQR). Models were adjusted for maximum of 1-hour ozone on the two prior days, allergy symptoms in the previous month, presence of cold or flu, asthma symptoms and inhaler use on the previous day, gender, day of the week and season.

We also examined associations of FeNO with PM_{10} from sources other than traffic exhaust. For this analysis we used the source-specific PM_{10} estimates from the PMF model described in Article 3. We defined two new sources: “traffic non-exhaust” by combining “road dust” with “tire & brake wear” contributions, and “mineral” by combining “mineral dust” with “construction” contributions. Models were adjusted for the same variables as described above.

Source-specific PM_{10} concentrations showed no statistically significant associations with FeNO (Figure 4–5). We observed positive trends for PM_{10} contributions from traffic exhaust, road salt, railway and mineral, while railway PM_{10} – together with road salt – showed smaller confidence intervals. Significant interactions were only found for inhaler use on the prior day with traffic exhaust and railway PM_{10}. On days without inhaler use, FeNO increased on average between 6-9% after increased traffic exhaust PM_{10}, while FeNO changes disappeared for railway PM_{10}. Nevertheless, all effects were statistically not significant.

These results have to be interpreted with caution. Source-specific PM_{10} concentrations were not available for all days of the health analysis, resulting in decreased power. In addition, the missing data were not evenly distributed over all children, which gave some children a stronger influence on the overall results.

Breath condensate nitrite

In contrast to FeNO, which is an inflammation marker of the upper airways, breath condensate nitrite is related to oxidative stress in the lower parts of the lungs. Therefore, nitrite from breath condensate was not correlated with FeNO (R^2=0.09). Yet, also for nitrite we observed the strongest effects for lag1 and lag1,2 air pollution. The following variables were included in the models: ambient NO, use of inhaler on same day, allergy symptoms in previous month, maximum of 1-hour ozone in the two prior days, temperature, day and season. In contrast to FeNO, there were no significant associations between traffic-related air pollution and breath condensate nitrite (Figure 4–6) and no interactions between air pollutants and the other variables were observed for this outcome.

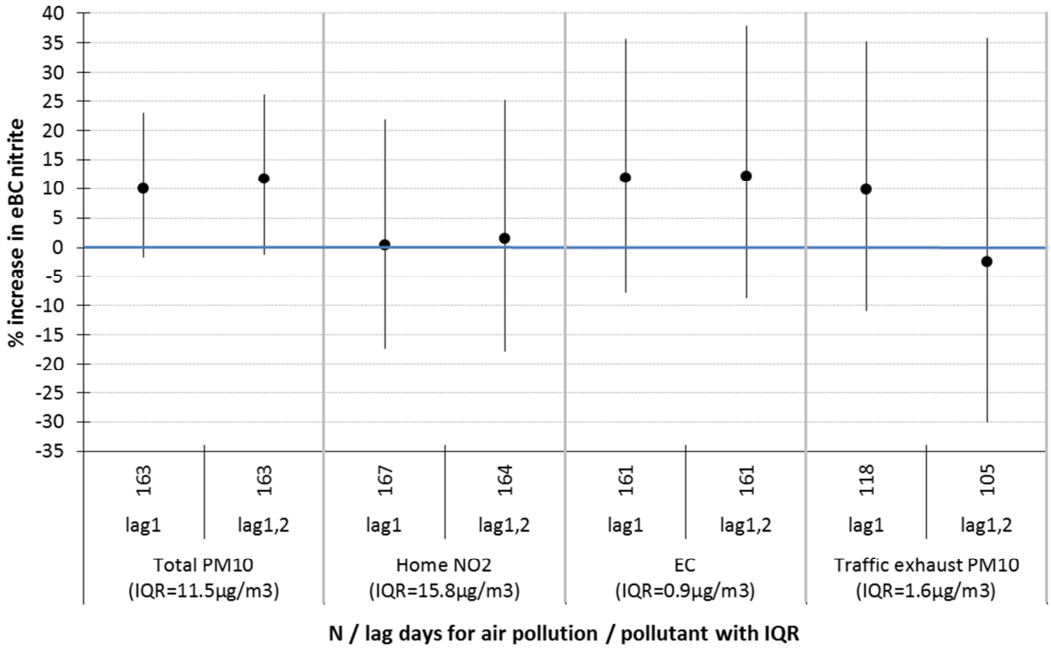


Figure 4–6: Average % increase (with 95% confidence interval) of breath condensate nitrite if air pollution concentrations at lag1 resp. lag1,2 were increased by the size of one interquartile range (IQR). Models were adjusted for ambient NO, use of inhaler on same day, allergy symptoms in previous month, maximum of 1-hour ozone in the two prior days, temperature, day and season.

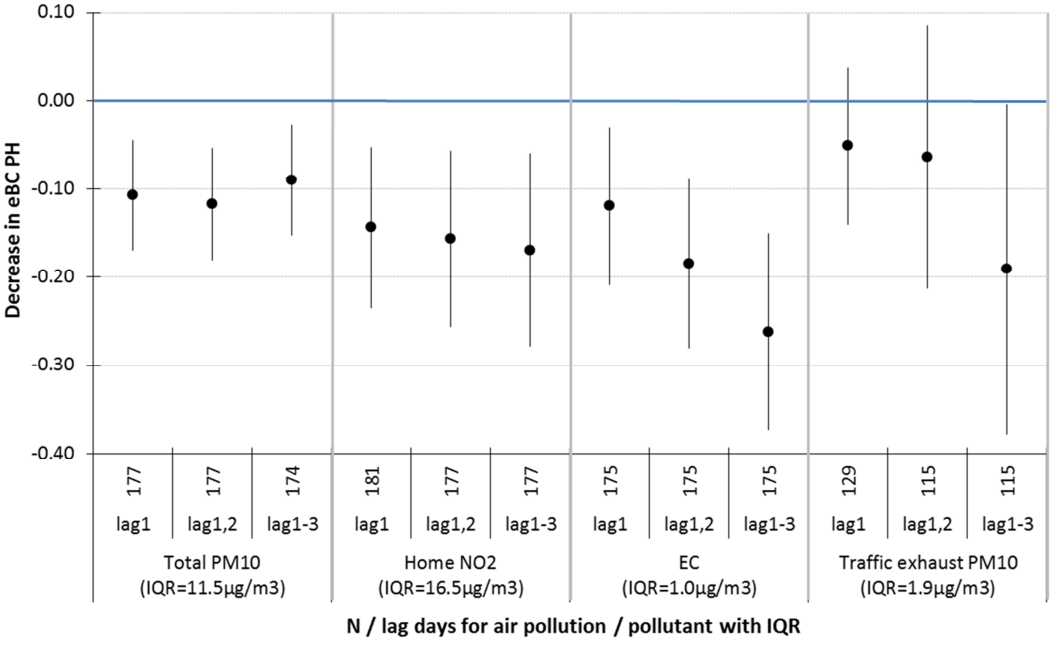


Figure 4–7: Average decrease (with 95% confidence interval) of breath condensate pH if air pollution concentrations at lag1, lag1,2 resp. lag 1-3 were increased by the size of one interquartile range (IQR). Models were adjusted for exposure to ETS in previous 24 hours, maximum of 1-hour ozone in the three prior days, day of the week, temperature and temperature squared.

Breath condensate pH

Breath condensate pH levels are also indicators of oxidative stress in the lower parts of the lungs. It is known that breath condensate pH levels in people with asthma are lower (pH <7, more acid) than in healthy people (pH >7, slightly alkaline) (Hunt et al., 2000). In the analysis of breath condensate pH, we included exposure to ETS in previous 24 hours, maximum of 1-hour ozone in the three prior days, day of the week, temperature and temperature squared. For all pollutants, higher concentrations on days preceding the health measurements were associated with a decrease in breath condensate pH (Figure 4–7). These associations were highly significant for total PM_{10}, home NO_2 and EC. For traffic exhaust-related PM_{10} we observed similar albeit not statistically significant trends.

Due to missing days in source-specific PM_{10} data and lower number of breath condensate measurements than for FeNO, we did not have enough statistical power to analyze the associations between source-specific PM_{10} and breath condensate nitrite or pH.

4.4. Discussion

We analyzed associations between traffic-related air pollution and markers of inflammation and oxidative stress in the lung. Significantly increased FeNO levels and decreased eBC pH levels were observed for increasing NO_2 and EC concentrations, while eBC nitrite showed no association with any of the pollutants.

Collection of FeNO and exhaled breath condensate are non-invasive methods to obtain levels of biomarkers related to inflammations in the lung. In recent years, FeNO has also been used for diagnosis and management of lung disease, as FeNO levels are known to be higher in asthmatics (Smith et al., 2005; Pijnenburg and De Jongste, 2008; Rodway et al., 2009). Average FeNO levels in the asthmatic children of our study were in the range of 7 to 44 ppb, comparable with mild asthma levels described in (Jatakanon et al., 1999).

We found the strongest positive associations for FeNO with the lag1 concentrations of NO_2 and EC. Total PM_{10} was not associated with FeNO. Similar results were reported by (Delfino et al., 2006). They studied FeNO in 45 children with asthma in California and found an increase in FeNO by 6.4% and 5.4% per interquartile range increment of lag1,2 personal exposure NO_2 and centrally measured EC, respectively. They also observed significant associations with personal but not with ambient $PM_{2.5}$.

Air pollution effects of home NO_2, EC and total PM_{10} in our study differed between person days with and person days without cold symptoms. On person days without cold symptoms, FeNO changes were significantly increased by 15%, 13% and 6% for increments of the amount of one IQR in lag1 NO_2, EC and total PM_{10}, respectively. In contrast, FeNO showed no such associations on person days with cold symptoms. Colds are connected with inflammation of the upper airways, which results in increased FeNO levels. These cold-related changes in FeNO are likely to be larger than the ones caused by air pollution and might thus mask these effects. We also found a significant modification of the association between PM_{10} and FeNO. according to the presence or absence of allergy symptoms in the month preceding the measurement. In contrast to other

studies (Koenig et al., 2003; Delfino et al., 2006), we could not find effect modifications by medication use for any of the pollutant variables considered.

Exhaled breath condensates of people with asthma have higher nitrite levels and lower pH (Hunt et al., 2000; van Beurden et al., 2002). However, only few studies have assessed short-term changes in exhaled breath condensate nitrite or pH in relation to air pollution variation (McCreanor et al., 2007; Laumbach and Kipen, 2010). We found significant acidification of the breath condensate following increased PM_{10}, home NO_2 or EC, whereas no association was present for breath condensate nitrite. In a recent study performed in young healthy adults at the Olympic Games in Beijing in 2008, Huang et al. (2012) observed large significant short-term changes in biomarkers for both, the pre to early Olympics period, when air pollution improved, and late to post Olympics period, when air pollution got worse again. They found significant positive associations of FeNO with $PM_{2.5}$, EC and NO_2, and significant negative associations of breath condensate pH levels with all pollutants considered and for different lag days. Breath condensate nitrite was also positively associated with pollutants, but significantly so only for NO_2.

With only thirteen children in the study and exposure data lacking on some days, statistical power was limited for the analysis of FeNO with source-specific PM_{10}. Moreover, source-specific estimates have some uncertainty from the modeling with positive matrix factorization. Therefore these results must be interpreted with caution. Nevertheless, we found positive albeit not significant associations between FeNO and coarser PM_{10} related to road salt and railway. Specific chemical elements might be responsible for these effects. These results are in line with those of a children asthma study (Gent et al., 2009), where they found significantly increased symptoms of wheezing, shortness of breath and chronic cough related to silicon (Si), iron (Fe), aluminum (Al) and Calcium (Ca). These chemical elements are also present in our profiles of road salt and especially in railway PM10. To get a better picture of source-specific effects on inflammatory markers, larger panel studies have to be done in the future.

4.5. References

Barraza-Villarreal, A., Sunyer, J., Hernandez-Cadena, L., Escamilla-Nuñez, M.C., Sienra-Monge, J.J., Ramírez-Aguilar, M., Cortez-Lugo, M., Holguin, F., Diaz-Sánchez, D., Olin, A.C., et al. (2008). Air Pollution, Airway Inflammation, and Lung Function in a Cohort Study of Mexico City Schoolchildren. Environ Health Perspect *116*, 832–838.

Bayley, D.L., Abusriwil, H., Ahmad, A., and Stockley, R.A. (2008). Validation of assays for inflammatory mediators in exhaled breath condensate. Eur Respir J *31*, 943–948.

van Beurden, W.J., Dekhuijzen, P.N., and Smeenk, F.W. (2002). Exhaled biomarkers in COPD: their potential role in diagnosis, treatment and prognosis. Monaldi Arch Chest Dis *57*, 258–267.

Brugge, D., Durant, J., and Rioux, C. (2007). Near-highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks. Environmental Health *6*, 23.

Delfino, R.J., Staimer, N., Gillen, D., Tjoa, T., Sioutas, C., Fung, K., George, S.C., and Kleinman, M.T. (2006). Personal and Ambient Air Pollution is Associated with Increased Exhaled Nitric Oxide in Children with Asthma. Environ Health Perspect *114*, 1736–1743.

FOEN (2003). Modelling of PM10 and PM2.5 ambient concentrations in Switzerland 2000 and 2010 (Bern: FOEN Federal Office for the Environment). Available at: http://www.bafu.admin.ch/publikationen/publikation/00258/index.html?lang=en.

FOEN (2004). Modelling of NO2 and benzene ambient concentrations in Switzerland 2000 to 2020 (Bern: FOEN Federal Office for the Environment). Available at: http://www.bafu.admin.ch/publikationen/publikation/00288/index.html?lang=en.

Gauderman, W.J., Vora, H., McConnell, R., Berhane, K., Gilliland, F., Thomas, D., Lurmann, F., Avol, E., Kunzli, N., Jerrett, M., et al. (2007). Effect of exposure to traffic on lung development from 10 to 18 years of age: a cohort study. The Lancet *369*, 571–577.

Gent, J.F., Koutrakis, P., Belanger, K., Triche, E., Holford, T.R., Bracken, M.B., and Leaderer, B.P. (2009). Symptoms and Medication Use in Children with Asthma and Traffic-Related Sources of Fine Particle Pollution. Environ Health Perspect *117*, 1168–1174.

Hazenkamp-von Arx, M.H., Schindler, C., Ragettli, M., Künzli, N., Braun-Fahrländer, C., and Liu, L.-J. (2011). Impacts of highway traffic exhaust in alpine valleys on the respiratory health in adults: a cross-sectional study. Environmental Health *10*, 13.

Ho, L.P., Innes, J.A., and Greening, A.P. (1998). Nitrite levels in breath condensate of patients with cystic fibrosis is elevated in contrast to exhaled nitric oxide. Thorax *53*, 680–684.

Horvath, I., Hunt, J., and Barnes, P.J., (2005). Exhaled breath condensate: methodological recommendations and unresolved questions. Eur Respir J *26*, 523–548.

Huang, W., Wang, G., Lu, S.-E., Kipen, H., Wang, Y., Hu, M., Lin, W., Rich, D., Ohman-Strickland, P., Diehl, S.R., et al. (2012). Inflammatory and Oxidative Stress Responses of Healthy Young Adults to Changes in Air Quality during the Beijing Olympics. Am. J. Respir. Crit. Care Med.

Hunt, J.F., Fang, K., Malik, R., Snyder, A., Malhotra, N., Platts-Mills, T. a. E., and Gaston, B. (2000). Endogenous Airway Acidification Implications for Asthma Pathophysiology. Am. J. Respir. Crit. Care Med. *161*, 694–699.

Jatakanon, A., Uasuf, C., Maziak, W., Lim, S., Chung, K.F., and Barnes, P.J. (1999). Neutrophilic Inflammation in Severe Persistent Asthma. Am. J. Respir. Crit. Care Med. *160*, 1532–1539.

Kelly, F.J., and Fussell, J.C. (2011). Air pollution and airway disease. Clinical & Experimental Allergy *41*, 1059–1071.

Koenig, J.Q., Jansen, K., Mar, T.F., Lumley, T., Kaufman, J., Trenga, C.A., Sullivan, J., Liu, L.J., Shapiro, G.G., and Larson, T.V. (2003). Measurement of offline exhaled nitric oxide in a study of community exposure to air pollution. Environ Health Perspect *111*, 1625–1629.

Laumbach, R.J., and Kipen, H.M. (2010). Acute effects of motor vehicle traffic-related air pollution exposures on measures of oxidative stress in human airways. Annals of the New York Academy of Sciences *1203*, 107–112.

McCreanor, J., Cullinan, P., Nieuwenhuijsen, M.J., Stewart-Evans, J., Malliarou, E., Jarup, L., Harrington, R., Svartengren, M., Han, I.-K., Ohman-Strickland, P., et al. (2007). Respiratory Effects of Exposure to Diesel Traffic in Persons with Asthma. N Engl J Med *357*, 2348–2358.

Perez, L., Rapp, R., and Kuenzli, N. (2010). The Year of the Lung: Outdoor air pollution and lung health. Swiss Medical Weekly. Available at:http://www.smw.ch/content/smw-2010-13129/.

Pijnenburg, M.W.H., and De Jongste, J.C. (2008). Exhaled nitric oxide in childhood asthma: a review. Clinical & Experimental Allergy *38*, 246–259.

Ragettli, M. (2009). Impacts of Exposure to Highway Air Pollution on Childhood Respiratory Health. Master Thesis. University of Basel.

Rodway, G.W., Choi, J., Hoffman, L.A., and Sethi, J.M. (2009). EXHALED NITRIC OXIDE IN THE DIAGNOSIS AND MANAGEMENT OF ASTHMA. Chron Respir Dis *6*, 19–29.

Rosias, P.P.R., Dompeling, E., Dentener, M.A., Pennings, H.J., Hendriks, H.J.E., Van Iersel, M.P.A., and Jöbsis, Q. (2004). Childhood asthma: Exhaled markers of airway inflammation, asthma control score, and lung function tests. Pediatric Pulmonology *38*, 107–114.

Smith, A.D., Cowan, J.O., Brassett, K.P., Herbison, G.P., and Taylor, D.R. (2005). Use of Exhaled Nitric Oxide Measurements to Guide Treatment in Chronic Asthma. New England Journal of Medicine *352*, 2163–2173.

Weinmayr, G., Romeo, E., De Sario, M., Weiland, S.K., and Forastiere, F. (2010). Short-Term Effects of PM10 and NO2 on Respiratory Health among Children with Asthma or Asthma-like Symptoms: A Systematic Review and Meta-Analysis. Environ Health Perspect *118*, 449–457.

5. Summary of the main findings

In the following, short summaries of the main findings that were discussed in detail in the respective articles and chapters are presented in relation to the research questions outlined in chapter 1.5.

Question 1: Can we predict residential outdoor exposure to different traffic-related air pollutants and are the estimates representative for personal exposure?

Southern California Study

Air pollution distribution

Air pollution levels and distribution were different in the two cities. Average outdoor $PM_{2.5}$ was much higher in Riverside than in Whittier with 28.3µg/m^3 and 16.7µg/m^3, respectively. Central and home outdoor OC and EC were also higher in Riverside compared to Whittier. Pollutant levels showed less variation across the microenvironments in Whittier.

Modeling and validation

City-specific and pooled models could explain a large part of variation for home outdoor $PM_{2.5}$, OC and EC with adjusted R^2 between 0.94 to 0.97, 0.80 to 0.91, and 0.75 to 0.87, respectively. The central site measurement was the predominant predictor in all models. Other important predictors were distance to highway or collector roads and wind variables. City-specific OC and EC models performed better than pooled models.

Daily personal $PM_{2.5}$ exposure correlated well with the predicted home outdoor $PM_{2.5}$ concentrations, with R^2s of 0.65, 0.69 and 0.69 for Riverside, Whittier and

both cities pooled. However, daily personal OC or EC exposure were poorly approximated by home outdoor estimates.

MfM-U study

Air pollution distribution

In Erstfeld, the traffic-related pollutants NO_2, EC and PN showed distinct spatial patterns with high concentrations at the highway site decaying some 30-40% to background levels within 150-200m. With 32.3µg/m^3, NO_2 concentrations at the highway site even exceeded the Swiss air quality standard of 30µg/m^3. In contrast, PM_{10} and OC were more homogeneously distributed. Weekday patterns of the traffic pollutants followed the heavy-duty truck traffic counts on the highway, while weekly levels related to meteorological conditions. All pollutants showed higher concentrations in winter than in summer.

Modeling and validation

A first prediction model, which did not include background measurements, explained 70% (adjusted R^2) of the NO_2 variation. Main predictors were stagnation index, temperature, and inverse distance weighted heavy-duty traffic counts. Inclusion of daily background NO_2 concentrations to this model explained an additional 21% of the variability in outdoor NO_2 concentrations. Model estimates matched very well the measured 14-day concentrations at the children's homes and additional community sites with an overall R^2 of 0.74.

Question 2: What are the different sources of PM10 in a highway impacted Alpine valley and how much do they contribute to ambient PM10?

Source contributions

In Erstfeld, nine sources were identified and apportioned using Positive Matrix Factorization (PMF). The main contributions to PM_{10} came from secondary particles (27%) and traffic (29%), which included traffic exhaust (18%), road dust (8%), tire & brake wear (1%), and road salt (2%). Other important sources were biomass burning (18%) and railway traffic (11%). The mineral sources, including mineral dust (7%) and construction site (6%), could not be split properly by PMF. The correlation between biomass burning estimates and measured levoglucosan, a marker for wood combustion, was very high with an R^2 of 0.81. The diesel exhaust marker 1-nitropyrine and the traffic exhaust estimates showed only a week association (R^2=0.13) due to the mixture of diesel and gasoline in the traffic fleet. There was a better correlation between NO_2, a more general traffic marker, and the traffic exhaust estimates (R^2=0.50).

Spatial and temporal distribution

The source contributions showed seasonal differences. In summer, when photochemical activity is highest, secondary particles (37%) was the major source, while in winter, biomass burning (26%) and traffic (30%) were more important. Although total PM_{10} concentrations were spatially homogeneous distributed, large differences could be observed for local traffic, railway and mineral contributions to PM_{10}, with higher contributions at sites close to the specific source.

Question 3: Are there any acute pulmonary health effects in children with asthma due to highway traffic-specific exposure?

Biomarker levels

The eight girls and five boys participating in the study had average fractional exhaled nitric oxide (FeNO), exhaled breath condensate (eBC) nitrite, and eBC pH levels of 17.04ppb, 0.82µM, and 7.06, respectively, indicative for mild asthma. Changes of these biomarkers related to traffic air pollution were assessed using total PM_{10} and EC concentrations at the highway site, home outdoor NO_2 estimates from the model described in Article 2, and source-specific PM_{10} from the PMF model described in Article 3. Effect estimates for air pollutants were scaled per inter quartile range (IQR).

Effects on FeNO

There was a not significant increase in FeNO of 6-8% per IQR increment of NO_2 and EC concentrations at lag1 and lag1,2. However, restricting the analysis on days when children reported no cold symptoms, FeNO significantly increased by 15%, 13% and 6% per IQR of lag1 NO_2, EC and total PM_{10}, respectively. Source-specific PM_{10} concentrations showed no significant associations with FeNO. However, there were positive trends for railway and road salt PM_{10}, also showing smaller confidence intervals than for other sources.

Effects on exhaled breath condensate

No significant associations between air pollution and eBC nitrite were observed. However, there was a significant acidification of eBC in relation to lag1, lag1,2 and lag1-3 PM_{10}, NO_2, and EC with decreases in pH levels of 0.09-0.12, 0.13-0.16, and 0.17-0.31, respectively.

6. General discussion

The findings presented in the present thesis provide new insights into air pollution distribution and sources in a rural Alpine setting, as well as into related acute changes in inflammatory biomarkers in children with asthma. In addition, modeling approaches were presented to improve the assessment of exposures. The following section puts these results in a more general context and discusses them in relation to existing literature.

6.1. Modeling challenges

One of the major challenges encountered in modeling traffic-related air pollution was the limited number of available monitoring stations: we had access only to 7 in Riverside and 8 both in Whittier and Erstfeld, excluding the background stations, while usual land-use regression models make use of at least 20, or better 40, measurement sites (Hoek et al., 2008). Therefore, we had a limited ability to capture the whole range of local characteristics by monitoring stations within the studied areas. To overcome this difficulty two different approaches were used. In the Southern California study, we added to the regression model the CALINE4 dispersion model estimates, which provided the spatial distribution of traffic-related air pollution. In the MfM-U study, adding similarly dispersion model estimates was not an option: estimates from the available Swiss PolluMap dispersion model (FOEN, 2003, 2004) have been shown to not accurately predict the air quality in Alpine regions (Liu et al., 2007). Emission inventories, which are essential in dispersion modeling, are usually limited for Alpine valleys. Additional challenges result from the specific topographical and meteorological conditions, such as the back and forth movements of pollutants transported by changing mountain wind systems or being trapped under inversion layers in winter (Harnisch et al., 2008; Gohm et al., 2009; Schnitzhofer et al., 2009). With the view to overcome this difficulty, we included three monitoring stations perpendicular to the highway at distances of 55m, 102m and 198m in order to capture traffic-related air pollution in Erstfeld. These approaches allowed us to

build spatially refined models with only a small set of monitoring sites. The performance of the models presented in this thesis is comparable to the performance of other reported land-use regression models (Hoek et al., 2008), with R^2s of the ratio models from 0.31 to 0.43 ($PM_{2.5}$) and 0.31 to 0.66 (EC) in the Southern California study, and an R^2 of 0.70 for the NO_2 model excluding the background site measurements in Erstfeld.

We used land-use regression modeling approaches to accommodate the locally different topographic, meteorological and air pollution distribution conditions at the three study sites. In the Southern California study for instance, important predictors retained in the OC and EC models for Riverside and Whittier were not identical. In Whittier, CALINE4 estimates were important predictors for EC, representing traffic contributions from the dense network of freeways, highways, and arterial roads. However in Riverside, with less road density, relative humidity and distance to highway were important. These local differences resulted in worse performance of the pooled models. A better performance of city-specific models was also shown in the SAPALDIA study in Switzerland, which compared eight communities in different regions (Liu et al., 2012). Area specific models performed better than the pooled models, especially for the Alpine communities Davos and Montana, emphasizing the need of small area models for complex topographic situations.

6.2. Distribution and sources of outdoor air pollution

The complex distribution of air pollution in an Alpine valley was previously described for the Inn valley in Austria (Harnisch et al., 2008; Gohm et al., 2009). Comparable topographic and meteorological conditions prevailed in our Erstfeld study. However, our source apportionment results showed that local sources can exert a major influence on air pollution distribution. Although monitoring stations were only a few hundred meters apart, we could observe noticeable differences in source contributions to PM_{10} (*e.g.* traffic exhaust, traffic non-exhaust, railway, construction site) between the various sites in Erstfeld. Such observations highlight the complex nature of local air pollution distribution in such an environment.

Highway traffic was clearly identified as a major air pollution source in Erstfeld. In particular, contributions from heavy-duty vehicles seem to be of importance. Air quality largely improved in Switzerland during the previous two decades (BAFU, 2012) because of drastic decreases in emissions from traffic vehicles (INFRAS, FOEN, 2012) resulting from the implementations of strict emission standards for new vehicles in the European Union and Switzerland, the so called Euronorm (European Commission, 2012). However, despite the advanced technologies used in new vehicles, emissions from diesel trucks are still higher than from passenger cars (diesel and gasoline), in particular NO_x emissions (INFRAS, FOEN, 2012). The fact that trucks affect the ambient air quality along highways could also be shown within the Erstfeld MfM-U study: indeed, the daily average air pollution levels for NO_2, EC and PN clearly matched the daily heavy-duty vehicle counts, although trucks only accounted for 14% of the total highway traffic (Article 2). Results are consistent with the findings of a relevant study on freeways in Los Angeles (Fruin et al., 2008). Variability in black carbon, NO, ultra-fine particles, and particle-bound polycyclic aromatic hydrocarbons measured directly on the freeway were explained by truck traffic density and not by the total traffic, even though trucks represented only 6% of the total traffic density. Such results emphasize the importance of the heavy-duty traffic contribution to ambient air pollution, and are of specific relevance for cargo traffic transit routes like the highway close to Erstfeld.

Contributions to PM_{10} from secondary particles, which originate partly from traffic sources, were almost as high as the direct contributions from traffic sources in Erstfeld. In Switzerland, PM_{10} contributions of nitrate-rich secondary particles increased during the last decade (Gianini et al., 2012). This is in part due to the strict emission standards for vehicles described above. New engine technologies and especially particle filters drastically decreased the amounts of emitted particles, although the level of reduction of NO_x precursor gases proved lower (INFRAS, FOEN, 2012). As a result, the share of secondary pollutants increased in the total PM_{10} levels. In the future, further technical improvements will lead to dynamic changes in the physico-chemical composition of air pollution, what should be closely monitored.

During winter time, biomass burning from residential heating was also an important source of PM_{10} in Erstfeld. In the literature, it is considered harmful for public health (Sarnat et al., 2008; Laumbach and Kipen, 2012). The contribution of biomass burning in Erstfeld was higher than in northern Switzerland, but similar to other Swiss Alpine communities with reported high biomass contributions (Szidat et al., 2007; Sandradewi et al., 2008; Gianini et al., 2012). An intervention study in Libby, Montana, where 1100 wood stoves were replaced by new low emission wood stoves, air quality improved and schoolchildren reported fewer respiratory health symptoms than before (Noonan et al., 2012).

6.3. Short-term health effects

There is rich literature dedicated to air pollution effects on children's lung functions and asthma symptoms (Health Effects Institute, 2010; Weinmayr et al., 2010). Few studies however, relate air pollution exposure to such inflammation markers as fractional exhaled nitric oxide (FeNO), and even fewer to exhaled breath condensate (eBC) biomarkers (Laumbach and Kipen, 2010). Measuring biomarkers in eBC is a relatively new method which still lacks standards in sample collection, storage and analysis procedures (Horvath et al., 2005; Chladkova et al., 2006; Kullmann et al., 2007; Vogelberg et al., 2008). Also, biomarker assays are commonly employed at or near their detection limits, leading to higher variability (Horvath et al., 2005). Often biomarkers cannot be quantified at all because of the high dilution in eBC. In our study for instance, cytokine levels were mostly below detection limit, as quoted in another study (Rosias et al., 2004).

Several studies looked at differences in biomarker levels between children with and without asthma (Franklin et al., 2003; Rosias et al., 2004; Ratnawati, 2006; Robroeks et al., 2007; Barraza-Villarreal et al., 2008; Pijnenburg and De Jongste, 2008), but few looked at the influence of short-term air pollution exposure on biomarker levels in children with asthma:

Air pollution effects on FeNO

We used modeled and fixed site air pollution concentrations for assessing acute changes in FeNO measurements within child. Only few studies looked at air pollution related FeNO changes using repeated measurements, and none of them used modeled home outdoor concentrations as exposure. However, two asthma panel studies used personal and/or measured outdoor air pollution concentrations. One of them was the Southern California study (see section 1.4), showing consistent results with the MfM-U study. Per inter quartile range (IQR) increase of lag1,2 NO_2 and EC, FeNO increased by 5.3% and 5.4% for central site measurements, and by 6.4% and 2.8% for personal measurements, respectively (Delfino et al., 2006). No significant association was found with PM_{10}. The other asthma panel study was in Seattle (Koenig et al., 2003) and reported that children not using an inhaler showed increased FeNO of 22%, 24.6%, 24.2%

and 25.7% per 10µg/m^3 increase of same day central, outdoor, indoor and personal $PM_{2.5}$, respectively. In a follow-up report (Koenig et al., 2005) only the estimated ambient-generated fraction of $PM_{2.5}$ was positively associated with FeNO (32%), but not the indoor-generated fraction.

Some asthma panel studies used hourly instead of daily exposure data. In Mexico, Barraza-Villarreal et al. (2008) carried out repeated measurements in 158 children with asthma and reported increases of 4.7%, 4.5% and 4.6% in FeNO per 8-hour moving average (IQR) $PM_{2.5}$, NO_2 and Ozone, respectively. (Mar et al., 2005) used a polynomial distributed lag model to examine hourly associations with FeNO levels in asthmatic children. They found that FeNO was only associated with hourly $PM_{2.5}$ up to 10-12 hours after exposure. This might explain the not significant results of PM_{10} by using daily lags in our study.

Other studies could not find any association between FeNO and air pollution levels (Holguin et al., 2007; Liu et al., 2009). However,(Holguin et al., 2007) reported increased FeNO levels of 28%, 27%, and 17% per IQR increment of road density within 50, 100, and 200 meter, respectively.

Air pollution effects on exhaled breath nitrite and pH

Several studies reported increased nitrite levels (Ho et al., 1998; Rosias et al., 2004) and decreased pH levels (Rosias et al., 2004; Hillas et al., 2011) in exhaled breath condensate in association to disease states such as asthma, COPD, and cystic fibrosis. To our knowledge no study assessed short-term changes in air pollution with exhaled breath nitrite and pH in children. However, there is one study of adults with asthma or COPD in four European cities (Manney et al., 2012) and another study with healthy young adults at the Olympic Games in Beijing (Huang et al., 2012). In the European study, the combined nitrite plus nitrate (NO_x) levels increased by 20.4% with an increase of 10µg/m^3 of the coarse part of PM ($PM_{2.5-10}$). No association was found for the other PM metrics. (Huang et al., 2012) reported significant nitrite changes of 10-20% per IQR of lag0 to lag5 NO_2, about 8% per IQR of lag 0 and lag3 $PM_{2.5}$, and about 10% per IQR of lag1 EC. Similar to our study, eBC pH levels decreased significantly for lag0 to lag5 $PM_{2.5}$ and EC. For NO_2, only lag1 and 2 were significant.

Source-specific exposure and health

The trend to use source-specific exposure is growing in research and a conference was convened about bridging the gap between sources and health outcomes (Solomon et al., 2012). Schlesinger et al. (2006) and Stanek et al. (2011) also reviewed the health relevance of particulate matter including the composition and characteristics of PM, the methodology, and the sources by looking at epidemiological and toxicological studies. They concluded that there is still a lack of studies using identifiable sources, *e.g.* through source apportionment, as exposure. Other studies looked at impacts from Saharan dust (Karanasiou et al., 2012) or biomass burning (Allen et al., 2008; Laumbach and Kipen, 2012; Noonan et al., 2012). However, to our knowledge, there is only one study linking multiple sources to asthma in children. Gent et al. (2009) used source apportionment to estimate source-specific exposure for 149 children with asthma. They found a 10% increased likelihood of wheeze for each 5 $\mu g/m^3$ increase in particles from motor vehicles, and a 28% increased likelihood of shortness of breath for increases in road dust. Neither of the other sources identified nor $PM_{2.5}$ alone was associated with increased health outcome risks. However, they found significantly increased symptoms of wheezing, shortness of breath and chronic cough related to silicon (Si), iron (Fe), aluminum (Al) and calcium (Ca). This was in line with our results, as these chemical elements were also present in our profiles of road salt and especially in railway PM_{10}, for which we found positive yet not significant trends in FeNO changes.

6.4. Strength and limitations

One of the strengths of the MfM-U study was its extensive database: over one and a half years of various daily air pollution measurements (*i.e.* NO_2, NO_x, PM_{10}, EC, OC, PN), chemical speciation data on daily PM_{10} filters, hourly traffic and meteorological data, as well as monthly measurements of inflammation and oxidative stress markers. In addition, levels of biomarkers (*i.e.* levoglucosan, 1-nitropyrene, 2-nitropyrene, 2-nitrofluoranthene) were recorded for comparison with specific source contributions from the PMF model. In the Southern California study, the strength of the work was the availability of the CALINE4 dispersion estimates and an extensive number of personal measurements (*i.e.* $PM_{2.5}$, EC, OC).

Despite the numerous repeated health marker measurements in Erstfeld, the sample of 13 children was relatively small, reducing the statistical power in the health analysis. A further limitation was that the central site in Riverside and the background site in Erstfeld were both partly affected by traffic, hence not providing reliable background air pollution levels. Furthermore, fractionated EC and OC data of one third of particle filters was not comparable anymore after a protocol change in the EC, OC analysis procedure. However, this fractionated data would have been useful to separate diesel and gasoline exhaust in the source apportionment analysis.

6.5. Conclusions and outlook

The results presented in this thesis underscore the significant influrence of traffic on both air quality and public health. Heavy-duty vehicles in particular affect the ambient air quality along highways. Children with asthma are specifically susceptible to short-term changes in traffic-related air pollution by responding with acute pulmonary inflammation episodes.

These findings support the Swiss “traffic relocation act” in force since 2001 which aims to reduce the heavy-duty traffic on the transalpine highways by moving the freight traffic to railways. Although, transalpine freight traffic declined from 1.4 to 1.2 million vehicles per year through different measures and incentives, the objective of 650’000 vehicles per year for 2017/18 remains far away.

In the future, it will be of special relevance to monitor the composition of air pollutants and carry out further investigations about their effects on health in order to overcome the present lack of information in this public-health area. Although improvements of technologies for vehicles, industry and appliances will probably lead to lower exposure levels to air pollution, they might also change the composition of the air pollution (*e.g.* more secondary pollution (Gianini et al., 2012)). Also introduction of new fuel types can alter the air pollution composition. All these changes might result in new health hazards.

On the exposure side, remote sensing data from satellites are promising for estimating short- or long-term air pollution concentrations. Satellite data largely improved in the last decade (Hoff and Christopher, 2009). There are even new approaches combining land-use regression models with remote sensing data to improve exposure models for epidemiological studies (Kloog et al., 2011).

One problem in air pollution monitoring is often the limited number of spatially distributed measurement sites. This issue might be solved by using existing infrastructure like tram and bus networks for measurement campaigns. Projects like OpenSence , which collect continuous data on trams in the city of Zürich, help to increase public awareness of environmental issues by posting real-time air pollution maps on the internet (OpenSense, 2012).

For large population studies, further developments in the smart phone sector might be the solution. Smart phones might even be used for multiple exposure studies, measuring for instance exposure to air pollution, noise and radio frequency radiation simultaneously (Kanjo et al., 2009; Maisonneuve et al., 2009).

7. References for chapters 1 & 6

Allen, R.W., Mar, T., Koenig, J., Liu, L.J.S., Gould, T., Simpson, C., and Larson, T. (2008). Changes in lung function and airway inflammation among asthmatic children residing in a woodsmoke-impacted urban area. Inhalation Toxicology *20*, 423–433.

Anderson, J., Thundiyil, J., and Stolbach, A. (2012). Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health. Journal of Medical Toxicology *8*, 166–175.

BAFU (2012). NABEL - Luftbelastung 2011. Messresultate des Nationalen Beobachtungsnetzes für Luftfremdstoffe (NABEL) (Bern: Bundesamt für Umwelt (BAFU)).

Barraza-Villarreal, A., Sunyer, J., Hernandez-Cadena, L., Escamilla-Nuñez, M.C., Sienra-Monge, J.J., Ramírez-Aguilar, M., Cortez-Lugo, M., Holguin, F., Diaz-Sánchez, D., Olin, A.C., et al. (2008). Air Pollution, Airway Inflammation, and Lung Function in a Cohort Study of Mexico City Schoolchildren. Environ Health Perspect *116*, 832–838.

Brandt, S. j., Perez, L., Künzli, N., Lurmann, F., and McConnell, R. (2012). Costs of childhood asthma due to traffic-related pollution in two california communities. European Respiratory Journal. Available at http://erj.ersjournals.com/content/early/2012/01/24/09031936.00157811.abstract.

Brauer, M. (2010). How Much, How Long, What, and Where. Proceedings of the American Thoracic Society *7*, 111 –115.

Brauer, M., Hoek, G., Smit, H.A., Jongste, J.C. de, Gerritsen, J., Postma, D.S., Kerkhof, M., and Brunekreef, B. (2007). Air pollution and development of asthma, allergy and infections in a birth cohort. Eur Respir J *29*, 879–888.

Brauer, M., Hoek, G., Van Vliet, P., Meliefste, K., Fischer, P., Gehring, U., Heinrich, J., Cyrys, J., Bellander, T., Lewne, M., et al. (2003). Estimating long-term average particulate air pollution concentrations: application of traffic indicators and geographic information systems. Epidemiology *14*, 228–239.

Brunekreef, B., and Holgate, S.T. (2002). Air pollution and health. Lancet *360*,

1233–1242.

Brunekreef, B., Janssen, N.A., De Hartog, J., Harssema, H., Knape, M., and Van Vliet, P. (1997). Air pollution from truck traffic and lung function in children living near motorways. Epidemiology *8*, 298–303.

California Air Resources Board California Ambient Air Quality Standards (CAAQS) (Sacramento, CA: California Environmental Protection Agency). Available at: http://www.arb.ca.gov/research/aaqs/caaqs/caaqs.htm.

Chen, L.C., and Lippmann, M. (2009). Effects of metals within ambient air particulate matter (PM) on human health. Inhal Toxicol *21*, 1–31.

Chladkova, J., Krcmova, I., Chladek, J., Cap, P., Micuda, S., and Hanzalkova, Y. (2006). Validation of Nitrite and Nitrate Measurements in Exhaled Breath Condensate. Respiration *73*, 173–179.

Dales, R., Liu, L., Wheeler, A.J., and Gilbert, N.L. (2008). Quality of indoor residential air and health. CMAJ *179*, 147–152.

Davidson, C.I., Phalen, R.F., and Solomon, P.A. (2005). Airborne Particulate Matter and Human Health: A Review. Aerosol Science and Technology *39*, 737–749.

Delfino, R.J., Staimer, N., Gillen, D., Tjoa, T., Sioutas, C., Fung, K., George, S.C., and Kleinman, M.T. (2006). Personal and Ambient Air Pollution is Associated with Increased Exhaled Nitric Oxide in Children with Asthma. Environ Health Perspect *114*, 1736–1743.

Delfino, R.J., Staimer, N., Tjoa, T., Gillen, D., Kleinman, M.T., Sioutas, C., and Cooper, D. (2008). Personal and Ambient Air Pollution Exposures and Lung Function Decrements in Children with Asthma. Environ Health Perspect *116*, 550–558.

Derom, E., Van Weel, C., Liistro, G., Buffels, J., Schermer, T., Lammers, E., Wouters, E., and Decramer, M. (2008). Primary care spirometry. Eur. Respir. J. *31*, 197–203.

European Commission (2012). Transport & Environment [online]. Available at: http://ec.europa.eu/environment/air/transport/road.htm.

European Parliament (2008). Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.

Available at: eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:

152:0001:0044:EN:PDF.

FOEN (2003). Modelling of PM10 and PM2.5 ambient concentrations in Switzerland 2000 and 2010 (Bern: FOEN Federal Office for the Environment). Available at: http://www.bafu.admin.ch/publikationen /publikation/00258/index.html?lang=en.

FOEN (2004). Modelling of NO2 and benzene ambient concentrations in Switzerland 2000 to 2020 (Bern: FOEN Federal Office for the Environment). Available at: http://www.bafu.admin.ch/publikationen/ publikation/00288/index.html?lang=en.

Franklin, P.J., Turner, S.W., Le Souef, P.N., and Stick, S.M. (2003). Exhaled nitric oxide and asthma: complex interactions between atopy, airway responsiveness, and symptoms in a community population of children. Thorax *58*, 1048–1052.

Fruin, S., Westerdahl, D., Sax, T., Sioutas, C., and Fine, P.M. (2008). Measurements and predictors of on-road ultrafine particle concentrations and associated pollutants in Los Angeles. Atmospheric Environment *42*, 207–219.

Gauderman, W.J., Vora, H., McConnell, R., Berhane, K., Gilliland, F., Thomas, D., Lurmann, F., Avol, E., Kunzli, N., Jerrett, M., et al. (2007). Effect of exposure to traffic on lung development from 10 to 18 years of age: a cohort study. The Lancet *369*, 571–577.

Gent, J.F., Koutrakis, P., Belanger, K., Triche, E., Holford, T.R., Bracken, M.B., and Leaderer, B.P. (2009). Symptoms and Medication Use in Children with Asthma and Traffic-Related Sources of Fine Particle Pollution. Environ Health Perspect *117*, 1168–1174.

Gianini, M.F.D., Fischer, A., Gehrig, R., Ulrich, A., Wichser, A., Piot, C., Besombes, J.-L., and Hueglin, C. (2012). Comparative source apportionment of PM10 in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation. Atmospheric Environment *54*, 149–158.

Gohm, A., Harnisch, F., Vergeiner, J., Obleitner, F., Schnitzhofer, R., Hansel, A., Fix, A., Neininger, B., Emeis, S., and Schäfer, K. (2009). Air Pollution Transport in an Alpine Valley: Results From Airborne and Ground-Based Observations. Boundary-Layer Meteorology *131*, 441–463.

Goswami, E., Larson, T., Lumley, T., and Liu, L.-J.S. (2002). Spatial

Characteristics of Fine Particulate Matter: Identifying Representative Monitoring Locations in Seattle, Washington. Journal of the Air & Waste Management Association *52*, 324–333.

Harnisch, F., Gohm, A., Fix, A., Schnitzhofer, R., Hansel, A., and Neininger, B. (2008). Spatial distribution of aerosols in the Inn Valley atmosphere during wintertime. Meteorology and Atmospheric Physics *103*, 223–235.

Hazenkamp-von Arx, M.H., Schindler, C., Ragettli, M., Künzli, N., Braun-Fahrländer, C., and Liu, L.-J. (2011). Impacts of highway traffic exhaust in alpine valleys on the respiratory health in adults: a cross-sectional study. Environmental Health *10*, 13.

Health Effects Institute (2010). HEI panel on the health effects of traffic-related air pollution. Traffic-related air pollution: a critical review of the literature on emissions, exposure, and health effects (Boston: Health Effects Institute). Available at: http://pubs.healtheffects.org/view.php?id=334.

Hillas, G., Kostikas, K., Mantzouranis, K., Bessa, V., Kontogianni, K., Papadaki, G., Papiris, S., Alchanatis, M., Loukides, S., and Bakakos, P. (2011). Exhaled nitric oxide and exhaled breath condensate pH as predictors of sputum cell counts in optimally treated asthmatic smokers. Respirology *16*, 811–818.

Ho, L.P., Innes, J.A., and Greening, A.P. (1998). Nitrite levels in breath condensate of patients with cystic fibrosis is elevated in contrast to exhaled nitric oxide. Thorax *53*, 680–684.

Hoek, G., Beelen, R., De Hoogh, K., Vienneau, D., Gulliver, J., Fischer, P., and Briggs, D. (2008). A review of land-use regression models to assess spatial variation of outdoor air pollution. Atmospheric Environment *42*, 7561–7578.

Hoff, R.M., and Christopher, S.A. (2009). Remote Sensing of Particulate Pollution from Space: Have We Reached the Promised Land? Journal of the Air & Waste Management Association *59*, 645–675.

Holguin, F., Flores, S., Ross, Z., Cortez, M., Molina, M., Molina, L., Rincon, C., Jerrett, M., Berhane, K., Granados, A., et al. (2007). Traffic-related Exposures, Airway Function, Inflammation, and Respiratory Symptoms in Children. Am. J. Respir. Crit. Care Med. *176*, 1236–1242.

Hopke, P.K. (2003). Recent developments in receptor modeling. Journal of

Chemometrics *17*, 255–265.

Horvath, I., Hunt, J., Barnes, P.J., and On behalf of the, A.T.S.E.R.S.T.F. o. E.B.C. (2005). Exhaled breath condensate: methodological recommendations and unresolved questions. Eur Respir J *26*, 523–548.

Huang, W., Wang, G., Lu, S.-E., Kipen, H., Wang, Y., Hu, M., Lin, W., Rich, D., Ohman-Strickland, P., Diehl, S.R., et al. (2012). Inflammatory and Oxidative Stress Responses of Healthy Young Adults to Changes in Air Quality during the Beijing Olympics. Am. J. Respir. Crit. Care Med. Available at: http://ajrccm.atsjournals.org/content/early/2012/08/29/rccm.201205-0850OC.

Hunt, J. (2007). Exhaled Breath Condensate—an overview. Immunol Allergy Clin North Am *27*, 587–v.

INFRAS, FOEN (2012). Switzerland's Informative Inventory Report 2012 (IIR) (Bern: INFRAS, BAFU). Available at: http://www.bafu.admin.ch/luft/11017/11024/11592/index.html.

Jerrett, M., Arain, A., Kanaroglou, P., Beckerman, B., Potoglou, D., Sahsuvaroglu, T., Morrison, J., and Giovis, C. (2004). A review and evaluation of intraurban air pollution exposure models. J Expo Anal Environ Epidemiol *15*, 185–204.

Jerrett, M., Burnett, R.T., Kanaroglou, P., Eyles, J., Finkelstein, N., Giovis, C., and Brook, J.R. (2001). A GIS - environmental justice analysis of particulate air pollution in Hamilton, Canada. Environment and Planning A *33*, 955–973.

Jerrett, M., Shankardass, K., Berhane, K., Gauderman, W.J., Künzli, N., Avol, E., Gilliland, F., Lurmann, F., Molitor, J.N., Molitor, J.T., et al. (2008). Traffic-Related Air Pollution and Asthma Onset in Children: A Prospective Cohort Study with Individual Exposure Measurement. Environ Health Perspect *116*, 1433–1438.

Kanjo, E., Bacon, J., Roberts, D., and Landshoff, P. (2009). MobSens: Making Smart Phones Smarter. IEEE Pervasive Computing *8*, 50 –57.

Karanasiou, A., Moreno, N., Moreno, T., Viana, M., De Leeuw, F., and Querol, X. (2012). Health effects from Sahara dust episodes in Europe: Literature review and research gaps. Environment International *47*, 107–114.

Kinney, P.L., and Nori-Sarma, A. (2011). White Paper: Health and Economic

Benefits of Clean Air Regulations | Joint Center for Political and Economic Studies. Available at: http://www.jointcenter.org/research/white-paper-health-and-economic-benefits-of-clean-air-regulations.

Kloog, I., Koutrakis, P., Coull, B.A., Lee, H.J., and Schwartz, J. (2011). Assessing temporally and spatially resolved PM2.5 exposures for epidemiological studies using satellite aerosol optical depth measurements. Atmospheric Environment *45*, 6267–6275.

Koenig, J.Q., Jansen, K., Mar, T.F., Lumley, T., Kaufman, J., Trenga, C.A., Sullivan, J., Liu, L.J., Shapiro, G.G., and Larson, T.V. (2003). Measurement of offline exhaled nitric oxide in a study of community exposure to air pollution. Environ Health Perspect *111*, 1625–1629.

Koenig, J.Q., Mar, T.F., Allen, R.W., Jansen, K., Lumley, T., Sullivan, J.H., Trenga, C.A., Larson, T., and Liu, L.J. (2005). Pulmonary effects of indoor- and outdoor-generated particles in children with asthma. Environ Health Perspect *113*, 499–503.

De Kok, T.M.C.M., Driece, H.A.L., Hogervorst, J.G.F., and Briede, J.J. (2006). Toxicological assessment of ambient and traffic-related particulate matter: A review of recent studies. Mutation Research/Reviews in Mutation Research *613*, 103–122.

Kuenzli, N., Perez, L., and Rapp, R. (2010). Air Quality and Health. Lausanne, Switzerland: ERS.

Kuenzli, N., and Tager, I.B. (2005). Air pollution: from lung to heart. Swiss Med Wkly *135*, 697–702.

Kullmann, T., Barta, I., and Horvath, I. (2007). Effect of freezing on exhaled breath condensate pH. Respiratory Medicine *101*, 2566.

Laumbach, R.J., and Kipen, H.M. (2010). Acute effects of motor vehicle traffic-related air pollution exposures on measures of oxidative stress in human airways. Annals of the New York Academy of Sciences *1203*, 107–112.

Laumbach, R.J., and Kipen, H.M. (2012). Respiratory health effects of air pollution: Update on biomass smoke and traffic pollution. Journal of Allergy and Clinical Immunology *129*, 3–11.

Liu, L., Poon, R., Chen, L., Frescura, A.-M., Montuschi, P., Ciabattoni, G., Wheeler, A., and Dales, R. (2009). Acute Effects of Air Pollution on

Pulmonary Function, Airway Inflammation, and Oxidative Stress in Asthmatic Children. Environ Health Perspect *117*, 668–674.

Liu, S.L.-J., Curjuric, I., Keidel, D., Heldstab, J., Künzli, N., Bayer-Oglesby, L., Ackermann-Liebrich, U., and Schindler, C. (2007). Characterization of Source-Specific Air Pollution Exposure for a Large Population-Based Swiss Cohort (SAPALDIA). Environ Health Perspect *115*, 1638–1645.

Liu, S.L.-J., Tsai, M.-Y., Keidel, D., Gemperli, A., Ineichen, A., Hazenkamp-von Arx, M., Bayer-Oglesby, L., Rochat, T., Künzli, N., Ackermann-Liebrich, U., et al. (2012). Long-term exposure models for traffic related NO2 across geographically diverse areas over separate years. Atmospheric Environment *46*, 460–471.

Maisonneuve, N., Stevens, M., Niessen, M.E., Hanappe, P., and Steels, L. (2009). Citizen noise pollution monitoring. In Proceedings of the 10th Annual International Conference on Digital Government Research: Social Networks: Making Connections Between Citizens, Data and Government, (Digital Government Society of North America), pp. 96–103.

Manney, S., Meddings, C.M., Harrison, R.M., Mansur, A.H., Karakatsani, A., Analitis, A., Katsouyanni, K., Perifanou, D., Kavouras, I.G., Kotronarou, N., et al. (2012). Association between exhaled breath condensate nitrate + nitrite levels with ambient coarse particle exposure in subjects with airways disease. Occup Environ Med *69*, 663–669.

Mar, T.F., Jansen, K., Shepherd, K., Lumley, T., Larson, T.V., and Koenig, J.Q. (2005). Exhaled Nitric Oxide in Children with Asthma and Short-Term PM2.5 Exposure in Seattle. Environ Health Perspect *113*, 1791–1794.

Morgenstern, V., Zutavern, A., Cyrys, J., Brockow, I., Gehring, U., Koletzko, S., Bauer, C.P., Reinhardt, D., Wichmann, H.E., and Heinrich, J. (2007). Respiratory health and individual estimated exposure to traffic-related air pollutants in a cohort of young children. Occup Environ Med *64*, 8–16.

Noonan, C.W., Ward, T.J., Navidi, W., and Sheppard, L. (2012). A rural community intervention targeting biomass combustion sources: effects on air quality and reporting of children's respiratory outcomes. Occup Environ Med *69*, 354–360.

OpenSense (2012). OpenSense [online].
Available at: http://www.opensense.ethz.ch/trac/.

Paatero, P. (1997). Least squares formulation of robust non-negative factor analysis. Chemometrics and Intelligent Laboratory Systems *37*, 23–35.

Paatero, P., and Tapper, U. (1994). Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics *5*, 111–126.

Pijnenburg, M.W.H., and De Jongste, J.C. (2008). Exhaled nitric oxide in childhood asthma: a review. Clinical & Experimental Allergy *38*, 246–259.

Pope, C.A., and Dockery, D.W. (2006). Health Effects of Fine Particulate Air Pollution: Lines that Connect. Journal of the Air & Waste Management Association *56*, 709–742.

Ragettli, M. (2009). Impacts of Exposure to Highway Air Pollution on Childhood Respiratory Health. Master Thesis. University of Basel.

Ratnawati, J.M.R.L.H.P.S.T. (2006). Exhaled breath condensate nitrite/nitrate and pH in relation to pediatric asthma control and exhaled nitric oxide. Pediatric Pulmonology *41*, 929–936.

Reff, A., Eberly, S.I., and Bhave, P.V. (2007). Receptor Modeling of Ambient Particulate Matter Data Using Positive Matrix Factorization: Review of Existing Methods. Journal of the Air & Waste Management Association *57*, 146–154.

Robroeks, C.M.H.H.T., Van De Kant, K.D.G., Jöbsis, Q., Hendriks, H.J.E., Van Gent, R., Wouters, E.F.M., Damoiseaux, J.G.M.C., Bast, A., Wodzig, W.K.W.H., and Dompeling, E. (2007). Exhaled nitric oxide and biomarkers in exhaled breath condensate indicate the presence, severity and control of childhood asthma. Clinical & Experimental Allergy *37*, 1303–1311.

Rosias, P.P.R., Dompeling, E., Dentener, M.A., Pennings, H.J., Hendriks, H.J.E., Van Iersel, M.P.A., and Jöbsis, Q. (2004). Childhood asthma: Exhaled markers of airway inflammation, asthma control score, and lung function tests. Pediatric Pulmonology *38*, 107–114.

Sandradewi, J., Prevot, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., and Baltensperger, U. (2008). A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer. Atmospheric Environment *42*, 101–112.

Sarnat, J.A., and Holguin, F. (2007). Asthma and air quality. Curr Opin Pulm Med

13, 63–66.

Sarnat, J.A., Marmur, A., Klein, M., Kim, E., Russell, A.G., Sarnat, S.E., Mulholland, J.A., Hopke, P.K., and Tolbert, P.E. (2008). Fine Particle Sources and Cardiorespiratory Morbidity: An Application of Chemical Mass Balance and Factor Analytical Source-Apportionment Methods. Environ Health Perspect *116*, 459–466.

Schlesinger, R.B., Kunzli, N., Hidy, G.M., Gotschi, T., and Jerrett, M. (2006). The health relevance of ambient particulate matter characteristics: coherence of toxicological and epidemiological inferences. Inhal Toxicol *18*, 95–125.

Schnitzhofer, R., Norman, M., Wisthaler, A., Vergeiner, J., Harnisch, F., Gohm, A., Obleitner, F., Fix, A., Neininger, B., and Hansel, A. (2009). A multimethodological approach to study the spatial distribution of air pollution in an Alpine valley during wintertime. Atmos. Chem. Phys. *9*, 3385–3396.

Seinfeld, J.H., and Pandis, S.N. (2006). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change (John Wiley & Sons).

Solomon, P.A., Costantini, M., Grahame, T.J., Gerlofs-Nijland, M.E., Cassee, F.R., Russell, A.G., Brook, J.R., Hopke, P.K., Hidy, G., Phalen, R.F., et al. (2012) Air pollution and health: bridging the gap from sources to health outcomes: conference summary. Air quality, atmosphere & health *5*, 9–62.

Stanek, L.W., Sacks, J.D., Dutton, S.J., and Dubois, J.-J.B. (2011). Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results. Atmospheric Environment *45*, 5655–5663.

Swiss Confederation (1998). Luftreinhalte-Verordnung.

Szidat, S., Prévôt, A.S.H., Sandradewi, J., Alfarra, M.R., Synal, H.-A., Wacker, L., and Baltensperger, U. (2007). Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophys. Res. Lett. *34*, L05820.

US EPA National Ambient Air Quality Standards (NAAQS) | Air and Radiation | US EPA (Washington DC, USA: US Environmental Protection Agency). Available at: http://www.epa.gov/air/criteria.html.

US EPA, O. (2012). London's Historic "Pea-Soupers" [online]. Available at:

http://www.epa.gov/aboutepa/history/topics/perspect/london.html.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., et al. (2008). Source apportionment of particulate matter in Europe: A review of methods and results. Journal of Aerosol Science *39*, 827–849.

Vogelberg, C., Kahlert, A., Wurfel, C., Marx, K., Bohm, A., Range, U., Neurneister, V., and Leupold, W. (2008). Exhaled breath condensate nitrite - methodological problems of sample collection. Medical Science Monitor *14*, CR416–CR422.

Weinmayr, G., Romeo, E., De Sario, M., Weiland, S.K., and Forastiere, F. (2010). Short-Term Effects of PM10 and NO2 on Respiratory Health among Children with Asthma or Asthma-like Symptoms: A Systematic Review and Meta-Analysis. Environ Health Perspect *118*, 449–457.

WHO (2006). Air quality guidelines. Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Available at: http://www.euro.who.int/en/what-we-do/health-topics/environment-and-health/air-quality/publications/pre2009/air-quality-guidelines.-global-update-2005.-particulate-matter,-ozone,-nitrogen-dioxide-and-sulfur-dioxide.

Zhu, Y.F., Hinds, W.C., Kim, S., Shen, S., and Sioutas, C. (2002). Study of ultrafine particles near a major highway with heavy-duty diesel traffic. Atmospheric Environment *36*, 4323–4335.

8. Appendices

Supplementary material to Article 1

Comparison between indoor and personal measurements

We compared the daily indoor measurements taken with Harvard Impactors (HI) with the daily averages of personal pDR measurements when the children spent more than 98% of the day at home indoors (8 days in Riverside, 11 days in Whittier). While measurements were about the same (slope: 0.75) in Riverside (Figure 1), we measured three times higher personal $PM_{2.5}$ than indoor concentrations (slope: 0.32) in Whittier (Figure 2).

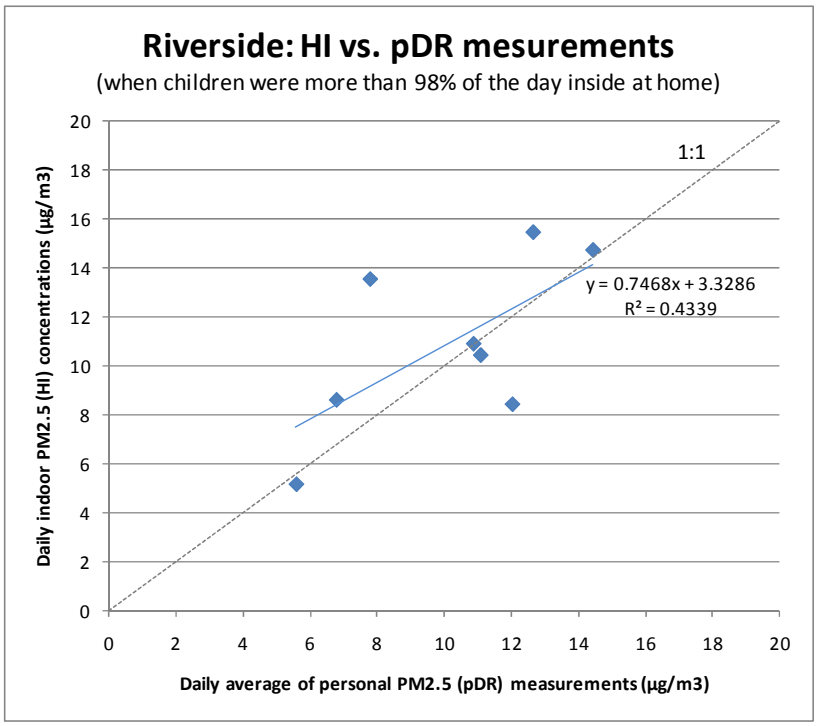


Fig. 1 Home indoor $PM_{2.5}$ measurements vs. personal $PM_{2.5}$ measurements when children were more than 98% of the day at home in Riverside

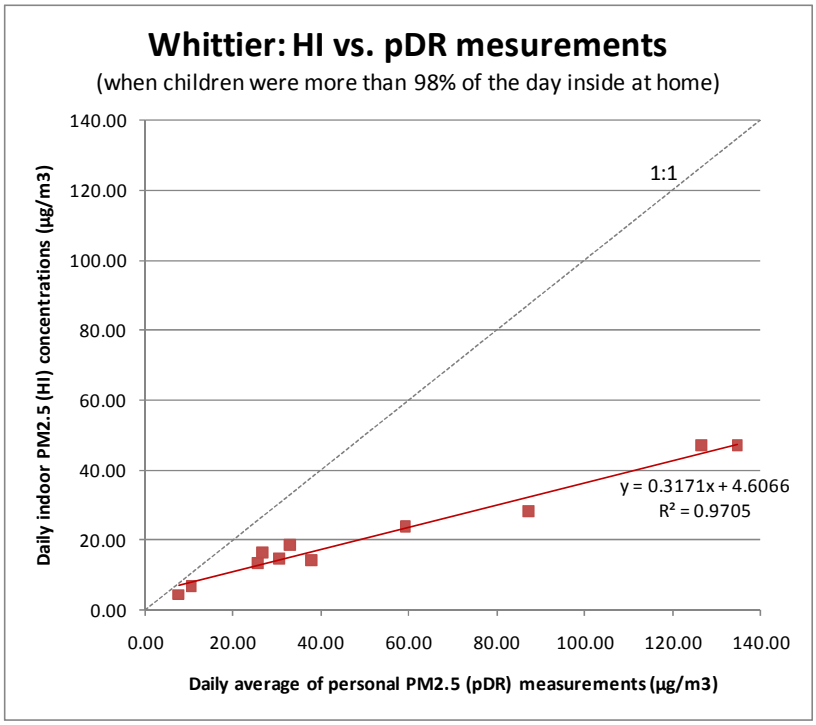


Fig. 2 Home indoor $PM_{2.5}$ measurements vs. personal $PM_{2.5}$ measurements when children were more than 98% of the day at home in Whittier

Supplementary material to Article 3

Table S1. Summary statistics and % of data below minimum detection limit (MDL) of species not included in PMF. (% below MDL>50% in bold)

Species	Mean	SD	MDL (ng/m^3)	% below MDL
Ag	1.47	0.58	2.69	**95**
As	0.69	0.57	0.29	31
Au	0.31	0.00	0.62	**100**
Cd	2.57	0.57	4.94	**97**
Ce	1.12	1.40	0.72	**60**
Co	1.37	2.52	0.29	**57**
Cs	0.93	1.75	0.72	**81**
Eu	1.09	1.79	1.10	**88**
Ga	0.42	0.24	0.67	**87**
Hf	1.06	0.90	1.30	**76**
Hg	0.32	0.19	0.53	**91**
In	2.27	0.96	4.08	**94**
Ir	0.66	0.12	1.30	**98**
La	0.66	1.04	0.67	**83**
Mo	1.70	1.83	0.77	39
Nb	0.40	0.22	0.67	**90**
P	23	15	0.58	1
Sb	5.67	14	7.73	**87**
Sc	0.93	1.68	0.34	**60**
Se	0.14	0.08	0.24	**92**
Sm	0.58	0.00	1.15	**100**
Sn	3.93	2.58	5.52	**80**
Sr	0.95	2.61	0.43	**62**
Ta	0.67	0.47	1.20	**96**
Tb	37	44	1.06	3
W	0.63	0.05	1.25	**100**
Y	0.35	0.25	0.48	**80**
Zr	2.59	3.07	0.58	28

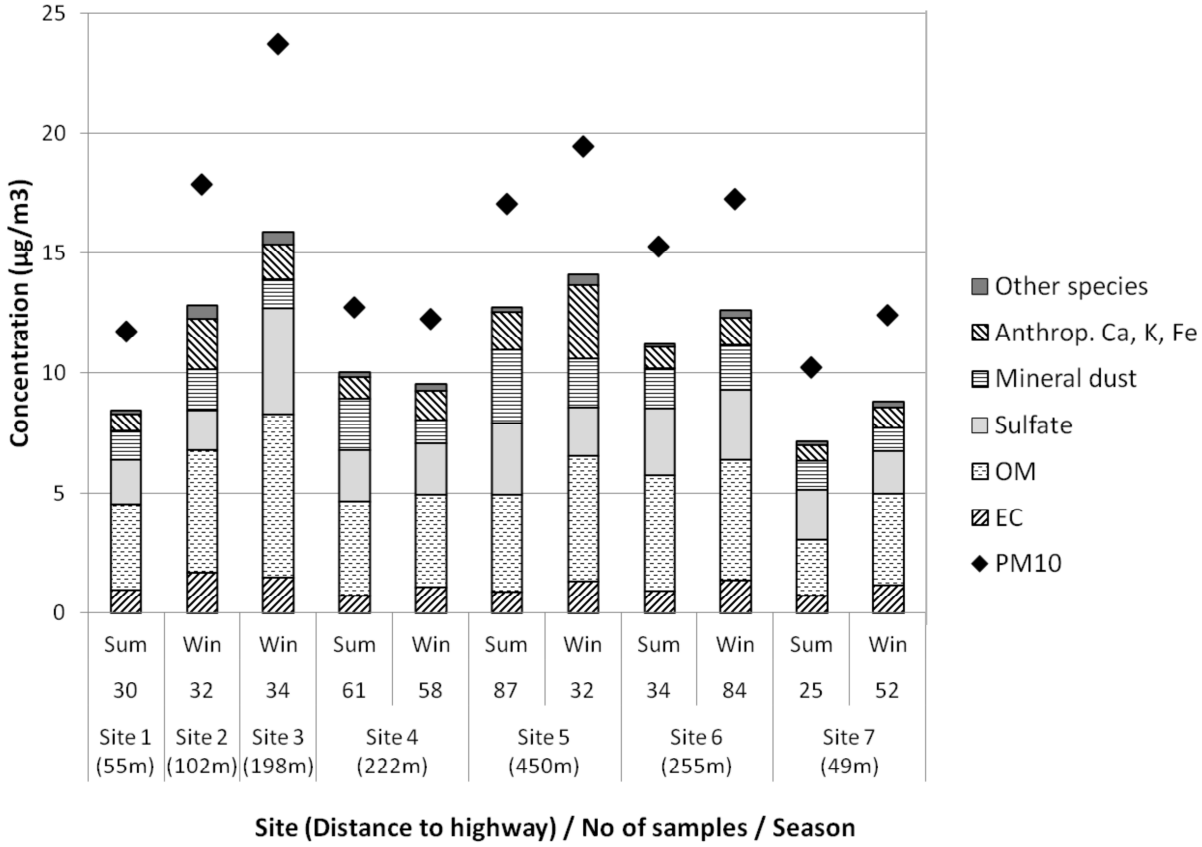


Fig. S1. Mass balance by site and season using reconstructed mass (RCM) as defined in Eq. 6.

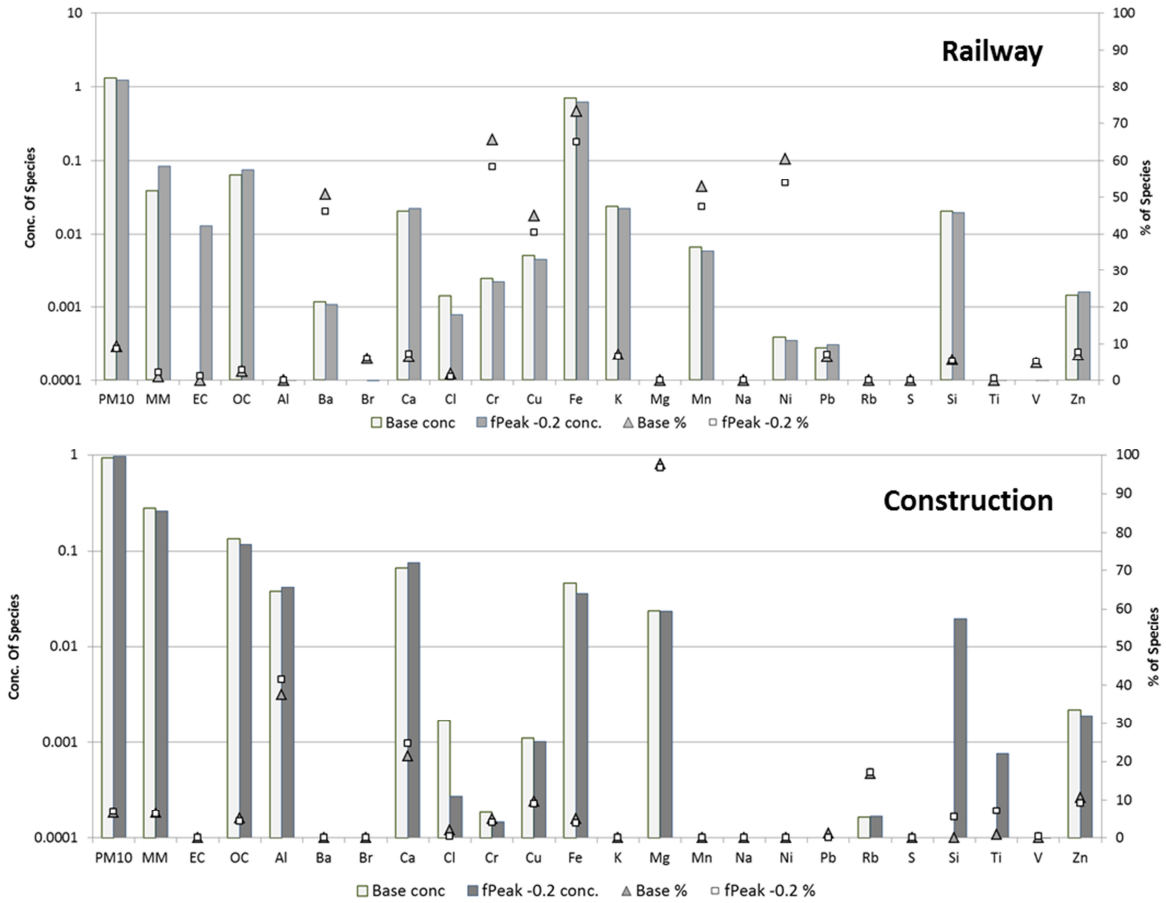


Fig. S2. Comparison of railway and construction site profiles obtained by Fpeak values 0 (Base) and -0.2.

An Fpeak value of -0.2 was chosen after reviewing *G space* plots and the different profiles. While *G space* plots were similar for the base (Fpeak = 0) and the Fpeak -0.2 models, the railway and construction site profiles showed differences. For the base model, EC was missing in the railway profile, although we know that diesel locks were used at the time of the study. In the construction site profile Si was missing, which is unrealistic due to the amount of minerals that were transported at this huge construction site. Therefore we chose an Fpeak value of -0.2 for our final model.

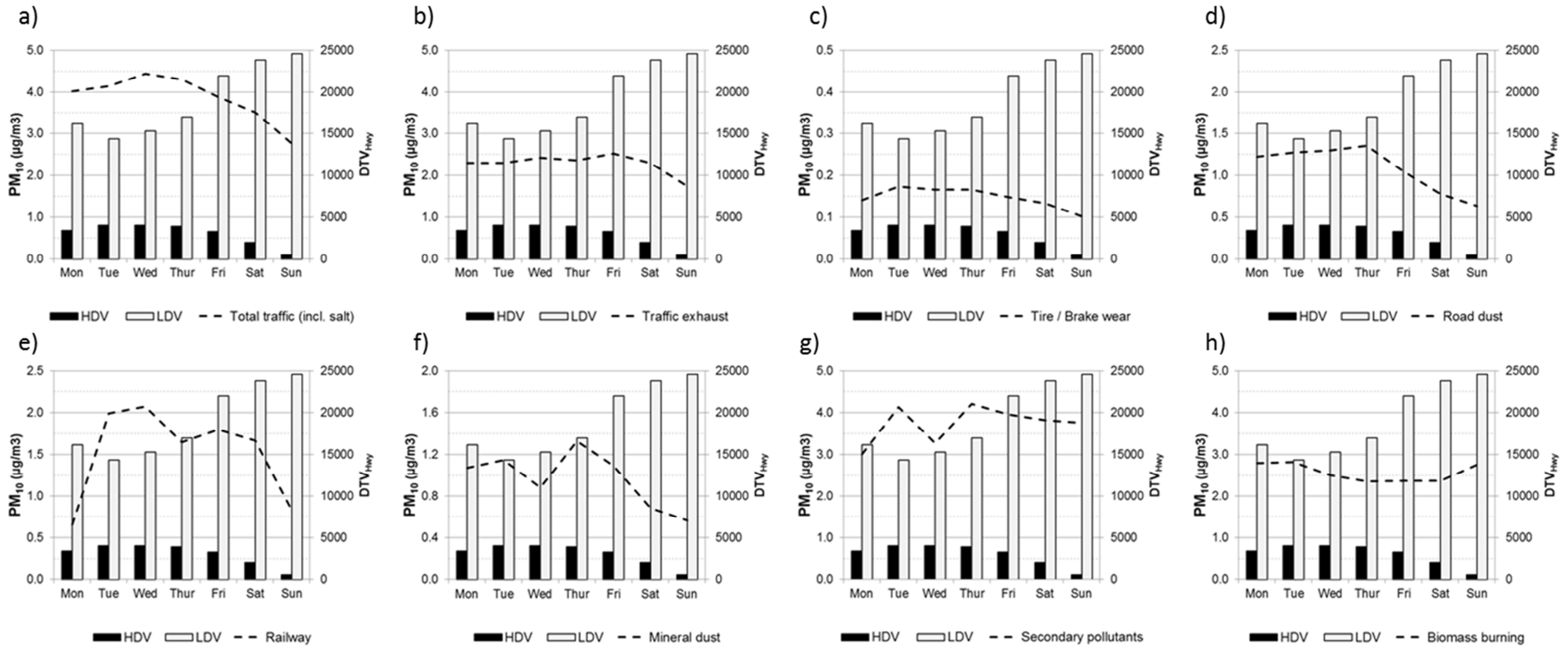


Fig. S3. PM_{10} source contributions by weekday compared with heavy-duty (HDV) and light-duty (LDV) traffic counts on the highway for the year 2008.

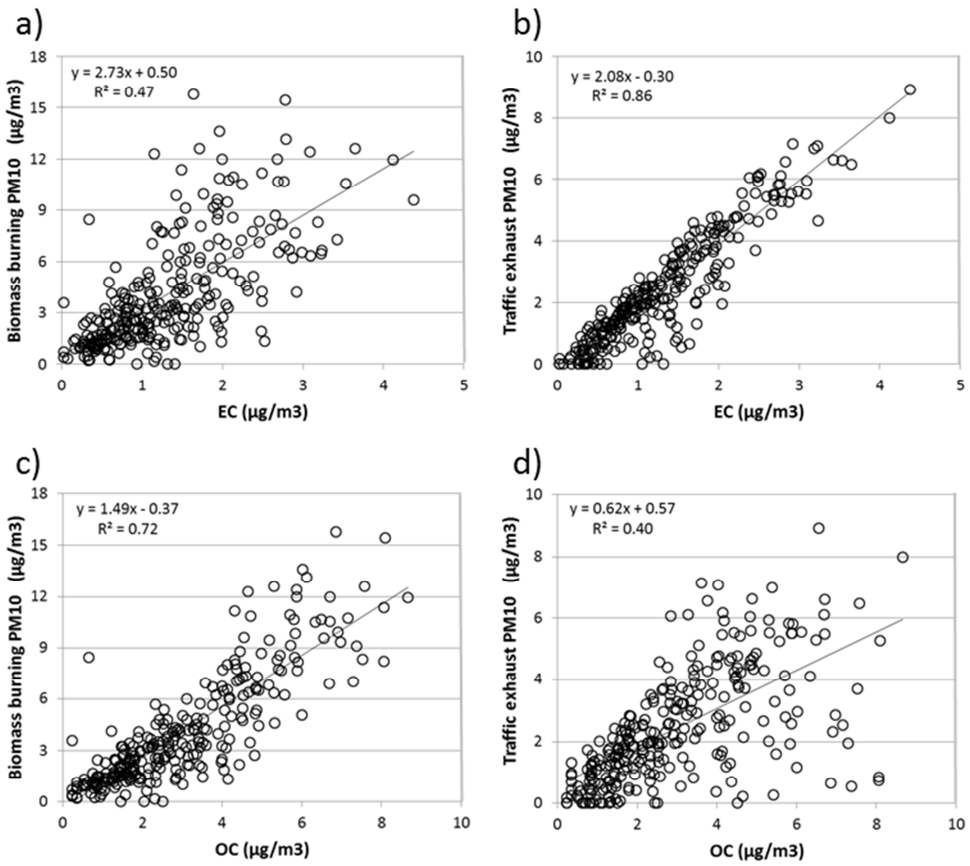


Fig. S4. Comparison of measured EC vs (a) biomass burning and (b) traffic exhaust; and measured OC vs (c) biomass burning and (d) traffic exhaust for daily winter data.

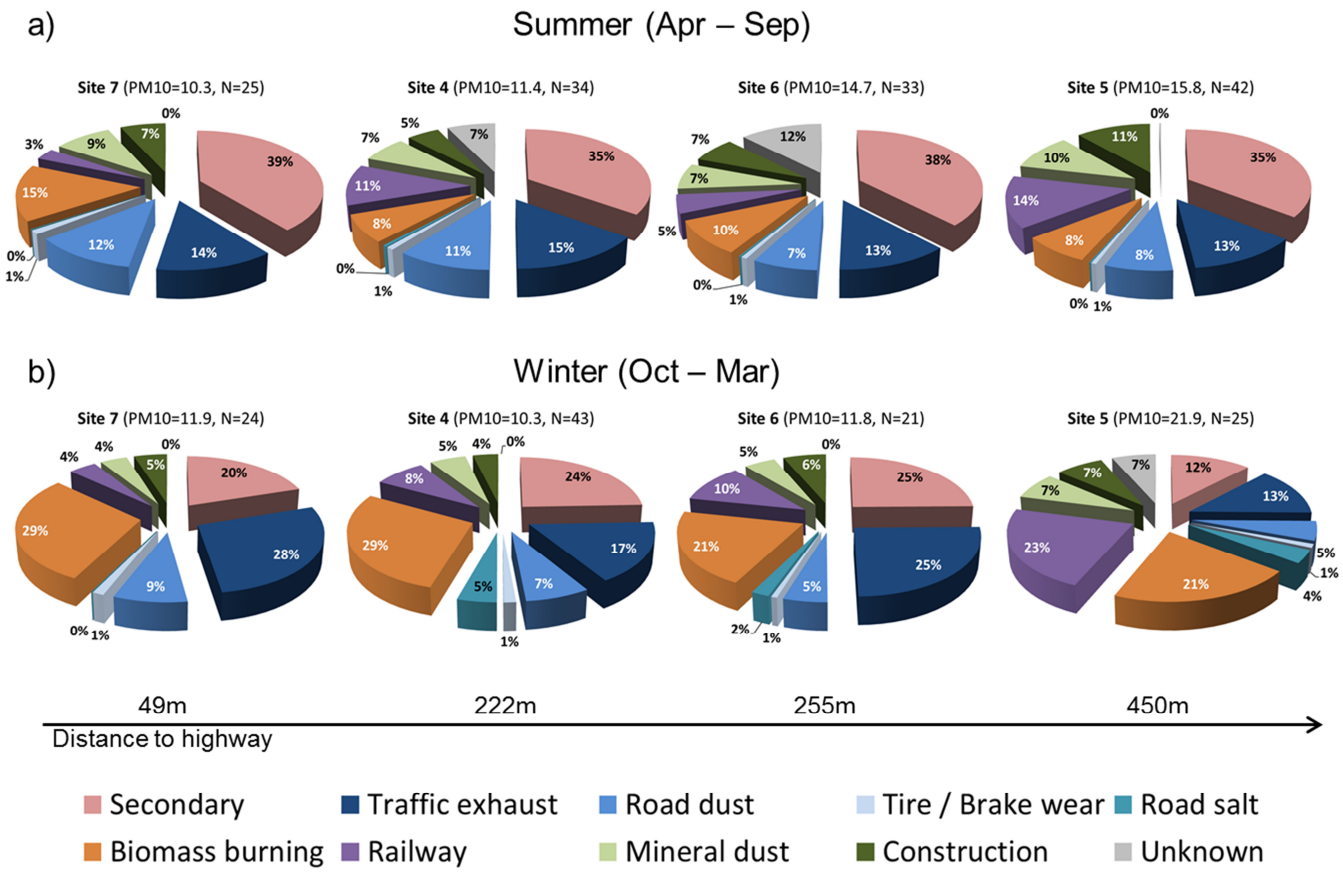


Fig. S5. Estimated source contributions by season for the four sites in the residential area. Note: Site 7 is protected by a tunnel and a noise barrier from the direct influence of the highway. Site 5 is closest to the railway and the construction site. Average daily PM10 conc. together with number of measurements at various site are presented in brackets.