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Analysis of Organic Molecular Markers in Airborne Particulate Matter: Application for Emission Source Apportionment

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Declaration on the Contribution to the Manuscripts for Cumulative Thesis

The following manuscripts were contributed by Raeed Megeed Qadir as a main author for the cumulative thesis and published in refereed scientific journals. The portion of Raeed Megeed Qadir of the work is represented in each case.

***Raeed Megeed Qadir**, Jürgen Schnelle-Kreis, Gülcin Abbaszade, Jose Manuel Arteaga-Salas,*
Jürgen Diemer and Ralf Zimmermann

Spatial and temporal variability of source contributions to ambient PM_{10} during winter in Augsburg, Germany using organic and inorganic tracers

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Raeed Megeed Qadir processed all data sets, performed the positive matrix factorization (PMF) analysis and wrote the paper. The laboratory analysis of organic compounds was performed by CMA group. The analyses of elements, inorganic ions, elemental and organic carbon were performed by Bavarian Environment Agency. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

***Raeed Megeed Qadir**, Gülcin Abbaszade, Jürgen Schnelle-Kreis, Judith Chow and Ralf Zimmermann*

Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany

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Raeed Megeed Qadir was responsible for the laboratory analysis of organic compounds and instrumental maintenance. He also performed the positive matrix factorization (PMF) analysis, processed all data sets and wrote the paper. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

The following manuscript was contributed by Raeed Megeed Qadir as a second main author for the cumulative thesis and accepted for publishing in refereed scientific journal. The portion of Raeed Megeed Qadir of the work is represented.

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Jürgen Orasche, Ralf Zimmermann and Lidia Morawska

Identification of the sources of primary organic aerosols at urban schools:
a molecular marker approach

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The laboratory analysis of organic compounds was performed by Raeed Megeed Qadir and other CMA group members. Raeed Megeed Qadir was responsible for proceeding and preparing data sets for the positive matrix factorization (PMF) analysis and he wrote the part of the paper which related to applying PMF model, results, interpretation and the discussion of PMF results. The final evaluation and interpretation of the results were performed in close cooperation with the co-authors.

München, April 2014

Raeed Megeed Qadir

“Ich werde meinen Namen an einem Ort verewigen wo berühmte Männer ihren Namen verewigt haben und wo bisher noch kein Mann seinen Namen verewigt hat”
GILGAMESCH

“I will set up my name in the place where the names of famous men are written, and where no man's name is written yet” *GILGAMESH*

I will set up my name in the place where the names of famous men are written, and where no man's name is written yet

GILGAMESH

For Who Changed My Life Once and Forever

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CONTENTS

ZUSAMMENFASSUNG

Der Inhalt dieser Dissertation befasst sich mit der umfassenden Analyse von organischen Spurenverbindungen und die Identifizierung der Emissionsquellen von luftgängigen Partikeln (particulate matter- PM). PM ist ein wichtiger Luftverschmutzungsindikator, der direkten Einfluss auf die menschliche Gesundheit hat. Viele im PM enthaltene Verbindungen werden damit in Verbindung gebracht. Zum Beispiel organische Verbindungen, wie polyzyklische aromatische Kohlenwasserstoffe (PAK), von denen viele karzinogen sind, aber auch Metalle und anorganische Salze, spielen eine wichtige Rolle. Sowohl PM_{10}, als auch $PM_{2.5}$ beinhalten inhalierbare Partikel, die mit neurodegenerativen, Atemwegs- und Herz-Kreislauf-Erkrankungen, als auch der Mortalität, korrelieren. In Deutschland wird die Minderung der Lebenserwartung aufgrund von Feinstaub auf neun bis zwölf Monate beziffert. Organische Verbindungen biogenen und anthropogenen Ursprungs können dabei bis zu 40% des Gesamtfeinstaubs ausmachen. Zum Schutz der Umwelt und der menschlichen Gesundheit sind umfangreiche wissenschaftliche Studien notwendig, um die Zusammensetzung des PM aus verschiedenen Quellen zu untersuchen. Deshalb werden seit vielen Jahren bereits organische Verbindungen zur Quellenidentifizierung eingesetzt.

Für diese Studie wurden PM-Proben gesammelt und mit einer neuen Methode, der in-situ-Derivatisierung-Thermodesorption-Gaschromatographie-Flugzeitmassenspektrometrie (IDTD-GC-ToF-MS) analysiert. In allen Fällen wurde die positive Matrix-Faktorisierung (PMF) eingesetzt; ein erweitertes Rezeptor-Modell für Quellenzuordnung. Damit wurden Quellenfaktoren für alle organischen und anorganischen Komponenten, die analysiert wurden, bestimmt, die eine anteilsmäßige Quellenzuordnung erlauben.

In der vorliegenden Arbeit wurden organische und anorganische Spurenverbindungen in PM_{10}-Proben von acht unterschiedlichen Probenahmeorten in Augsburg wurden analysiert. Die jeweiligen Anteile wurden dazu verwendet um die räumliche und zeitliche Variabilität der Emissionsquellen zu bestimmen. Die PMF erlaubte eine Identifizierung von neuen Quellenfaktoren. So zeigte sich, dass der Faktor für Holzverbrennung in einer Wohnsiedlung mit 5.1 $\mu g/m^3$ am stärksten ausgeprägt war. Straßenstaub und Straßenbahn hatten ihren höchsten Anteil an einem Verkehrsknotenpunkt (16.2 $\mu g/m^3$) sowie an einem anderen Punkt in der Innenstadt (6.6 $\mu g/m^3$). Der PMF-Faktor für sekundäres Sulfat und sekundäres Nitrat waren an allen Probenahmestationen ähnlich ausgeprägt (im Schnitt 6.2 bzw. 4.3 $\mu g/m^3$). In München wurden $PM_{2.5}$-Proben vor und nach Einführung der Umweltzone (Low Emission Zone-LEZ) gesammelt, um die Auswirkungen der LEZ zu untersuchen. Es zeigte sich, dass sich der Einfluss der meisten organischen Verbindungen nach der Einführung der LEZ verringerte. Mit Hilfe der PMF konnten hier fünf Hauptfaktoren Emissionsquellen zugeordnet werden. Der Anteil des Verkehrsfaktors verringerte sich dabei durch die Einführung der LEZ um 60%. So schrumpfte beispielsweise der Anteil von elementarem Kohlenstoff (elemental carbon-EC) aus Verkehrsemissionen von 1.1 auf 0.5 $\mu g/m^3$. Abschließend beschäftigt sich diese Dissertation mit der Identifizierung der organischen Spurenverbindungen aus lokalen (hauptsächlich Verkehr) und regionalen Quellen (überwiegend Biomasseverbrennung), die in $PM_{2.5}$-Proben untersucht wurden, die an elf unterschiedlichen Schulen in Brisbane, Australien, gesammelt wurden. Diese Feinstaub-Quellen beeinflussen damit direkt die Luftqualität an den unterschiedlichen Schulen und letztlich wie stark die Schüler PM ausgesetzt werden. Insgesamt konnten mit der PMF und den organischen Spurenverbindungen vier unterschiedliche Quellen identifiziert werden: Fahrzeugemissionen, Biomasseverbrennung, Fleischzubereitung und Pflanzenwachse. Den höchsten Anteil an den Schulen zeigte mit 45% organisch gebundener Kohlenstoff (organic carbon-OC) der Fahrzeugemissionen. Die Biomasseverbrennung hatte einen saisonal stark schwankenden Anteil von 29% an OC. Im Winter war dieser Anteil aufgrund von Buschfeuer rund um Brisbane am höchsten. Das Zubereiten von Fleisch hatte einen Anteil von 16% am OC, möglicherweise auch durch die Mensen vor Ort bedingt. Pflanzenwachse trugen mit mindestens 7% zum organischen Kohlenstoff bei.

ABSTRACT

The extent of this thesis covers the comprehensive analysis of organic molecular markers and identifying of the emission sources in in airborne particulate matter (PM). PM is one of the most important air pollutants that adversely influence human health. Many components of PM are currently seen as responsible for health effects, for instance organics such as PAH that are known carcinogens and directly toxic to the cells, as well as metals and inorganic salts. Both PM_{10} and $PM_{2.5}$ include inhalable particles and the impact effects of inhalable PM are well correlated to the increase in respiratory, neurodegenerative and cardiovascular diseases as well as mortality. In Germany, the average loss of life expectancy due to respiratory diseases and lung malfunctions attributable to PM is about nine to twelve months. Organic compounds of biogenic and anthropogenic origin often represent a large fraction, up to 40%, of total airborne PM mass and influence the behavior and impact of PM on human health. To protect both human health and the environment, comprehensive studies necessary to evaluate the composition of PM at the different emission sources. Therefore, organic compounds have been used as source indicators in aerosol research for many years and several studies have used organic compounds for source apportionment.

The PM samples were analyzed for their organic constituents by applying a recently developed method of the in-situ derivatization -thermal desorption-gas chromatography- time of flight mass spectrometry (IDTD GC-ToF-MS). In all cases, Positive Matrix Factorization (PMF); an advanced receptor model of source apportionment has been applied to all obtained data of POC and inorganics to identify the possible sources and associated contributions.

The organic and inorganic tracers have been analyzed in PM_{10} samples, collected over a one-month sampling campaign at eight sampling sites in Augsburg, Germany. The contribution of organic and inorganic tracers to PM_{10} samples was estimated to evaluate the spatial and temporal variation of emission sources at the sampling sites. The results showed that PMF was able to identify nine source factors depending on the organic and inorganic tracers. Organic and inorganic tracers of wood combustion for example showed that the maximum daily average contribution at a residential site (5.1 $\mu g/m^3$). Other tracers of road dust & tram source were detected with the maximum daily average contribution factor at a traffic site (16.2 $\mu g/m^3$) and urban site (6.6 $\mu g/m^3$). On the other hand, secondary sulfate and secondary nitrate factors had approximately similar contributions (6.2 and 4.3 $\mu g/m^3$, respectively) at all sites. While the analysis of the organic molecular markers in $PM_{2.5}$ samples, collected within the low emission zone (LEZ) of Munich, Germany, showed that the concentration for most of the organic compounds has been decreased after the implementation of the LEZ. Applying of PMF model in this case was able to identify five source factors depending on the concentration of organic compounds. It was noticed that the contribution of traffic source factor decreased about 60% after the implementation of the LEZ. Thus, the average concentration of EC in the traffic factor decreased from 1.1 to 0.5 $\mu g/m^3$. Furthermore, analysis of organic molecular markers in $PM_{2.5}$ samples, collected at 11 different schools in Brisbane Australia, has been used to identify the local (traffic) and regional (biomass burning) primary sources. These primary detected sources influence the levels of ambient particles that children are exposed at school, which has implications when considering potential controls to mitigate exposure at schools. The results showed that the application of PMF identified four sources; vehicle emissions, biomass burning, meat cooking and plant wax using organic molecular markers data. At the schools studied, highest overall contributions were attributed to vehicle emissions; about 45% of the organic carbon (OC). Biomass burning was the second largest source accounting for 29% of the OC with an observed seasonal trend that peaked in winter due to prescribed burning of bush land around Brisbane. Meat cooking emissions accounted for 16% of the OC, possibly from school canteens while plant wax emissions had minimum contributions (7% of the OC).

1. INTRODUCTION

1.1 Particulate Matter

An aerosol is generally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 10^{-9}–10^{-4} m (lower limit: molecules and molecular clusters; upper limit: rapid sedimentation) [1, 2]. Particulate Matter (PM) is a widespread air pollutant, consisting of a mixture of solid and liquid particles suspended in the air. Commonly used measures describing PM that are relevant to health refer to the mass concentration of particles with an aerodynamic diameter of less than 10µm (PM_{10}) and of particles with an aerodynamic diameter of less than 2.5µm ($PM_{2.5}$). PM includes "inhalable coarse particles," with diameters larger than 2.5µm and smaller than 10µm and "fine particles," with diameters that are 2.5µm and smaller. PM also comprises ultrafine particles having a diameter of less than 0.1µm. In most locations in Europe, $PM_{2.5}$ constitutes 50–70% of ambient PM_{10} [3]. Particles between 0.1µm and 1µm in diameter can remain in the atmosphere for days or weeks and thus are subject to long-range transboundary transport in the air [4].

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Particles can either be directly emitted into the air (primary PM) or be formed in the atmosphere from gaseous precursors such as sulfur dioxide, oxides of nitrogen, ammonia and non-methane volatile and semi volatile organic compounds (secondary PM). PM is a mixture with physical and chemical characteristics varying with location and time. Common chemical constituents of PM include sulfates, nitrates, ammonium, other inorganic ions such as ions of sodium, potassium, calcium, magnesium and chloride, crustal material, particle-bound water, metals (including cadmium, copper, nickel, vanadium and zinc), elemental carbon and organic compounds [3]. Moreover, airborne particles play an important role in the spreading of biological organisms, reproductive materials, and pathogens (pollen, bacteria, spores, viruses, etc.) and they can cause or enhance respiratory, cardiovascular, infectious and allergic diseases [2].

Primary and secondary PM can have both man-made (anthropogenic) and natural (non-anthropogenic) sources. Primary particles are directly emitted as liquids or solids from anthropogenic sources such as fossil fuel (coal, lignite, heavy oil and biomass) combustion for energy production in households and industry, combustion engines (both diesel and gasoline), other industrial activities (building, mining, manufacture of cement, ceramic and bricks and smelting), and erosion of the pavement by road traffic and abrasion of brakes and tyres (traffic-related suspension of road dusts). Nowadays, ships are considered as one of the main sources of PM. For example, the average of particle emissions from ships in average emissions factors of 0.33 and 1.34 g/kWh for different types of fuel [5].The natural source of primary PM includes: volcanic eruptions, soil, mineral dust, sea salt and biological materials (plant fragments, microorganisms, pollen, etc.). Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere (new particle formation by nucleation and condensation of gaseous precursors on to particles) [2]. Anthropogenic sources of secondary particles include the atmospheric transformation of nitrogen oxides (traffic and some industrial processes), ammonia (mainly emitted by agricultural activities) and sulfur dioxide resulting from the combustion of sulfur-containing fuels. While soil and dust re-suspension are the natural source of particles, particularly in arid areas or during episodes of long-range transport of dust, for example from the Sahara to southern Europe [3]. After biogenic sources in summer months of Central Europe (temperatures < 25 °C), wood combustion sources and cold starting motor vehicles are two of the major emission sources of volatile organic compounds(VOC) during winter periods which leads to the formation of secondary organic aerosol (SOA) [6, 7].

The chemical composition of ambient PM varies considerably and consists of many different compounds [8]. The organic constituents of airborne particles influence the behavior and impact of PM on human health, regional visibility and global climate [9]. Organic compounds of biogenic and anthropogenic origins often represent a large fraction, up to 40%, of total PM mass [10] and the concentrations of organic compounds are ranging from below pg/m^3 to $\mu g/m^3$ [11]. In an urban environment primary sources of particles can include vehicle emissions, biomass burning (from both domestic and open fires), coal combustion, cooking, plant abrasion and paved road dust. For these primary sources there are a number of organic markers that are known to be characteristic of a specific emission source and crucially also have a long lifetime in the atmosphere to enable detection at monitoring stations [12]. Examples of some of the more specific organic markers include levoglucosan for biomass burning [13] and cholesterol for meat cooking [14]. Hopanes are present in fossil fuels, and the different hopanoid compounds are specific to the different types of fossil fuels such as coal or petroleum and lubricating oil [15] (and references therein). Thus these organic compounds along with others can be used as molecular markers for identifying the contributing primary sources to ambient particles. To develop effective emission control strategies and to protect both human health and the environment, it is important to combat pollutant emissions at the source and identify and implement the most effective reduction measures at local, national and international levels. Comprehensive studies are therefore necessary to evaluate the characteristics of PM at the different sources [16]. Therefore, inorganics and organic compounds have been used as source indicators in aerosol research for many years and several studies have used organic compounds for source apportionment [12, 17-23].

Airborne particulate matter, which includes dust, dirt, soot, smoke and liquid droplets emitted into the air, is small enough to be suspended in the atmosphere and so called aerosol. Airborne PM is complex mixture of solid and liquid particles of primary and secondary origin, which contain a wide range of inorganic and organic components. They can be characterized by their physical attributes (mass, size and optical properties), which influence their transport, deposition and impact on climate, and their chemical composition, which influences their effect on health and climate. PM mass and composition is highly variable in spatial- temporal terms and is, beside emission strengths, strongly influenced by meteorological conditions. Primary PM can be emitted from both natural and man-made sources, including forest fires, dust storms, traffic and industry, and is found both outdoors and indoors. In terms of the latter, PM may be generated within the built environment or may be transported from outside via various mechanisms. Typically, PM is defined according to the aerodynamic diameter of the particles which make up a particular fraction, as this is what determines how long they will reside in the air, how far they may be transported and, in terms of health, how they will be deposited in the respiratory system [24]. Fig.1 shows the size distribution of particulate matter adapted from Vallero, 2010 [25].

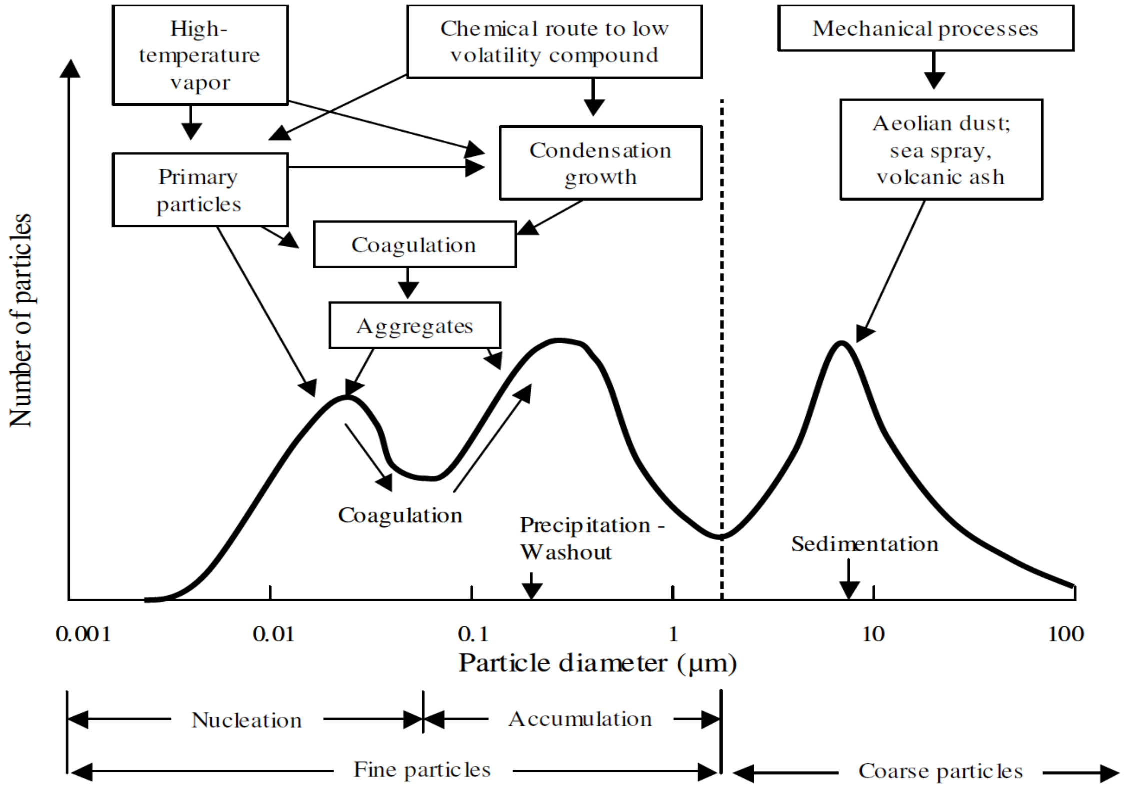


Figure 1. Prototypical size distribution of particulate matter with selected sources and pathways of how the particles are formed.

Particles interact with various substances in the air to form organic or inorganic chemical compounds. For example, small anthropogenic particles like soot or fly ash are adsorbed to surfaces of larger minerals [26] as shown in Fig.2 which has been adapted from Schleicher et. al., 2010. The most common combinations of fine particles are those with sulfate [27]. The smaller particles contain the secondarily formed aerosols, combustion particles, re-condensed organic and metal vapors. The carbonaceous component of fine particles (products of incomplete combustion and secondary organic aerosol formation) contains both elemental carbon (graphite and soot) and organic compounds (emitted e.g. in combustion exhaust and secondary organic compounds formed by photochemistry). Additionally, atmospheric reactions of nitrogen oxides produce nitric acid vapor (HNO_3) that may accumulate as nitrate particles in both fine and coarse forms. The most common combination of coarse particles consists of oxides of silicon, aluminum, calcium and iron [28].

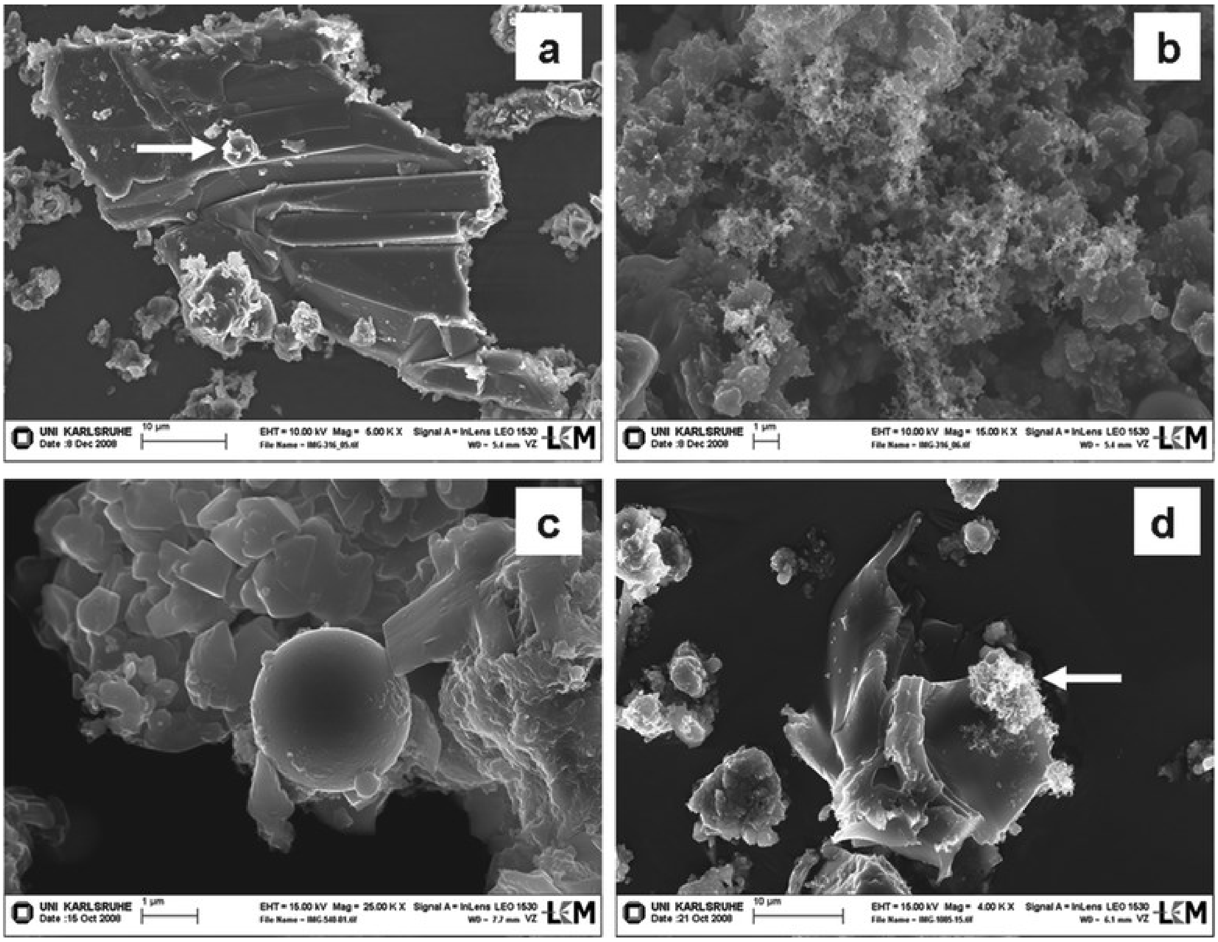


Figure 2. Typical examples for particle interactions in Beijing TSP samples. (a) anthropogenic carbon particle with sharp edges together with minerals and a small fly ash (Mg–Al–Oxide; white arrow); (b) soot chains covering the surfaces of larger particles; (c) aluminium silica oxide fly ash (spherical particle) on gypsum; (d) carbon particle with soot (white arrow) on its surface. Figure is adapted from Schleicher et. al., 2010, Institute of Mineralogy and Geochemistry, University of Karlsruhe (TH), Adenauer Ring 20, 76131 Karlsruhe, Germany.

1.2 Exposure to PM and Health Effects

The linkages and associations between air pollution and health are determined largely through epidemiological studies. Epidemiological and toxicological studies have shown that PM mass comprises different fractions with varying types and degrees of adverse health effects, suggesting a role for both the chemical composition and physical properties of PM [29]. Many components of PM attached to black carbon are currently seen as responsible for health effects, for instance organics such as PAH that are known carcinogens and directly toxic to the cells, as well as metals and inorganic salts[3]. Recently, the exhaust from diesel engines (consisting mostly of particles) was classified by the International Agency for Research on Cancer (IARC) as carcinogenic (Group 1) to humans based on sufficient evidence that exposure is associated with an increased risk for lung cancer [30]. This list also includes some PAHs and related exposures, as well as the household use of solid fuels [3] (and references therein).The World Health Organization (WHO) estimated that exposure to fine particulate air pollution caused 800,000 deaths and 6.4 million lost years of healthy life in the world's cities in 2000 [31]. The ambient air quality for few regions has improved considerably in the last few decades. However, there is convincing evidence that current levels of air pollution still pose a considerable risk to the environment and to human health. PM is one of the most important air pollutants that adversely influences human health [32]. Long term exposure to PM_{10} and $PM_{2.5}$ has been associated with effects on breathing and the respiratory system, lung tissue damage, cancer and both cardiovascular mortality and morbidity. Comprehensive epidemiological and toxicological evidence indicates that there are consistent associations between increased risk of adverse health outcomes and exposure to PM [33, 34]. Both PM_{10} and $PM_{2.5}$ include inhalable particles that are small enough to penetrate the thoracic region of the respiratory system. The health effects of inhalable PM are well documented and appreciable body of data suggests a significant increase in respiratory, neurodegenerative and cardiovascular diseases as well as mortality after both short- and long-term exposure to atmospheric PM [35, 36]. They are due to exposure over both the short term (hours, days) and long term (months, years) and include:

- Respiratory and cardiovascular morbidity, such as aggravation of asthma, respiratory symptoms and an increase in hospital admissions.

- Mortality from cardiovascular and respiratory diseases and from lung cancer.

There is good evidence of the effects of short-term exposure to PM_{10} on respiratory health, but for mortality, and especially as a consequence of long-term exposure, $PM_{2.5}$ is a stronger risk factor than the coarse part of PM_{10}. All-cause daily mortality is estimated to increase by 0.2-0.6% per 10 $\mu g/m^3$ of PM_{10} [37]. Long-term exposure to $PM_{2.5}$ is associated with an increase in the long-term risk of cardiopulmonary mortality by 6–13% per 10 $\mu g/m^3$ of $PM_{2.5}$ [38, 39]. Exposure to $PM_{2.5}$ also reduces the life expectancy of the population of the region by about 8.6 months on average [3].

Many of the health endpoints may result, at least in part, from oxidative stress initiated by the formation of reactive oxygen species (ROS) at the surface of and within target cells [40, 41]. ROS is a collective term representing chemically reactive oxygen radicals or oxygen-derived species (e.g. hydroxyl radical and hydrogen peroxide) [42]. While ROS is continually formed in the human body as a natural byproduct of aerobic metabolism, high levels of ROS can cause a change in the redox status of the cell, leading to severe responses such as pulmonary inflammation and, at higher concentrations, apoptosis [41, 43].

Specific health outcomes associated with cellular oxidative stress include the ability of PM to induce pro-inflammatory effects in the nose, lung and cardiovascular system [40]. Susceptible groups with pre-existing lung or heart disease, as well as elderly people and children, are particularly vulnerable. For example, exposure to PM affects lung development in children, including reversible deficits in lung function as well as chronically reduced lung growth rate and a deficit in long-term lung function [44]. There is no evidence of a safe level of exposure or a threshold below which no adverse health effects occur. The exposure is ubiquitous and involuntary, increasing the significance of this determinant of health. It is estimated that approximately 3% of cardiopulmonary and 5% of lung cancer deaths are attributable to PM globally. In the European region, this proportion is 1-3% and 2-5%, respectively, in various sub regions [31].

In Germany for example, the average loss of life expectancy due to respiratory diseases and lung malfunctions attributable to particles is about nine to twelve months. Although the health importance of aerosols is well known, there is still a lack of knowledge on the question which aerosol fraction or property is responsible for the observed health effect. This research gap is the main motivation which has been addressed by the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosols and Health (HICE). HICE works on a better understanding of the negative effects of anthropogenic aerosols on human health. Nowadays, more investigations in the domain of health effects of ship emissions, wood and coal combustion are conducted by HICE. The Helmholtz Zentrum München - German Research Center for Environmental

Health, the University of Rostock and a large number of national and international partners cooperate in HICE (http://www.hice-vi.eu/).

WHO reported in its recent report entitled “Health Effect of Particulate Matter” in 2013 [3], that there is evidence that decreased levels of particulate air pollution following a sustained intervention result in health benefits for the population assessed. These benefits can be seen with almost any decrease in level of PM. The health and economic impacts of inaction should be also assessed.

1.3 Spatial and Temporal Variability of PM

In recent years, there has been growing interest in the exposure and health implications of living near major roadways as well as in related questions of whether some locations have systematically higher concentrations than others for health relevant pollutants. As a result, rapid growth of literature describing analysis of the spatial and temporal variations in observed pollutant concentrations [45] (and references therein). Characterization of the spatial and temporal variation in PM composition is crucial in order to enable a thorough understanding of the formation, transport and accumulation of PM in the atmosphere; such knowledge is important for air quality monitoring and management [46] and potential for the misclassification of population-average ambient exposures of communities exists due to spatial variability of PM concentration when a limited number of ambient PM monitors are used [21].

1.3.1 Spatial Variability

Ambient concentrations of particles vary spatially to differing degrees depending on size fraction, largely because the terminal settling time for particles increases rapidly with particle size [47]. For particles with a diameter larger than 1.0µm, terminal settling velocity is proportional to the square of the diameter of the particle [48], or in other words, the smaller the particle, the more homogeneous its distribution. Stopping distance, or the distance a particle travels when ejected from a source, is one property that provides an explanation as to why larger particle classes travel shorter distances, creating more spatial heterogeneity in an intraurban setting [47]. However, a common assumption is that the spatial distributions of certain pollutants, especially smaller particulates, are homogeneously distributed within large urban areas and that the concentrations between sites are well correlated [47, 49].

The dispersion and transportation phenomenon of PM in the atmosphere is the prime concern for the air pollution researchers. Once emitted into the atmosphere, primary and secondary aerosol particles are carried and dispersed by atmospheric motion over a wide range of scales, and deposited on the ground at distances ranging from several to hundreds of kilometers from the emission point. The dispersion and transportation of PM is affected by various meteorological parameters such as wind speed, relative humidity, wind direction, temperature, etc. The dispersion of pollutants is dependent on their downwind transport by the prevailing wind [50] (and references therein).

The interpretation of spatial contrasts of PM concentrations is limited by differences in site selection and differences of sampling and analysis methods including different correction factors used to compensate for sampling losses of volatile components between countries and network operators [21]. The assessment of spatial variability of PM in the terms of uniformity and heterogeneity distribution was reviewed and discussed in detail by Wilson et. al., 2005 [49]. Fig.3 shows the global spatial map of fine $PM_{2.5}$ distribution over land [51], and high concentrations are evident in South and East Asia. High concentrations (annual averages >50 μg/m^3) are also apparent in North Africa, Central Asia, and Saudi Arabia, which result primarily from airborne mineral dust, rather than combustion emissions [52]. Several studies in the United States and Great Britain found long-term mean $PM_{2.5}$ and PM_{10} concentrations to be uniformly distributed within an urban environment, whereas a higher variability within-city was observed for the coarse fraction [53]. While in China, personal exposure average mass concentrations of PM ranged from 58.6 to 73.5 μg/m^3, and were not always lower than the outdoor concentrations which averaged 80.5 μg/m^3 [54]. The major sources of pollutant emissions include motor vehicles and industrial sources. Economic growth has fueled both. From the year 2000 to 2004, the passenger car fleet more than doubled in China, as China's population benefited from increased income. Industrial plants contribute much of the dust and soot in China. The United Nations Development Program in 2002 estimated that the death rate from lung cancer in severely polluted areas of China was 4.7-8.8 times higher than in areas with good air quality [54, 55] indicating the spatial variation between different cities of China. The spatial variability of $PM_{2.5}$ components across the United States (US) was studied by Bell et. al., 2007[56] and it was found that the $PM_{2.5}$ concentration in the western region of US (average >6 μg/m^3) is almost 2-time more than eastern region (average 3 μg/m^3). In addition, they reported that there was a northeast decreasing levels towards the southeast for some components of $PM_{2.5}$ and the north/south gradient remains throughout all seasons for other components of $PM_{2.5}$.

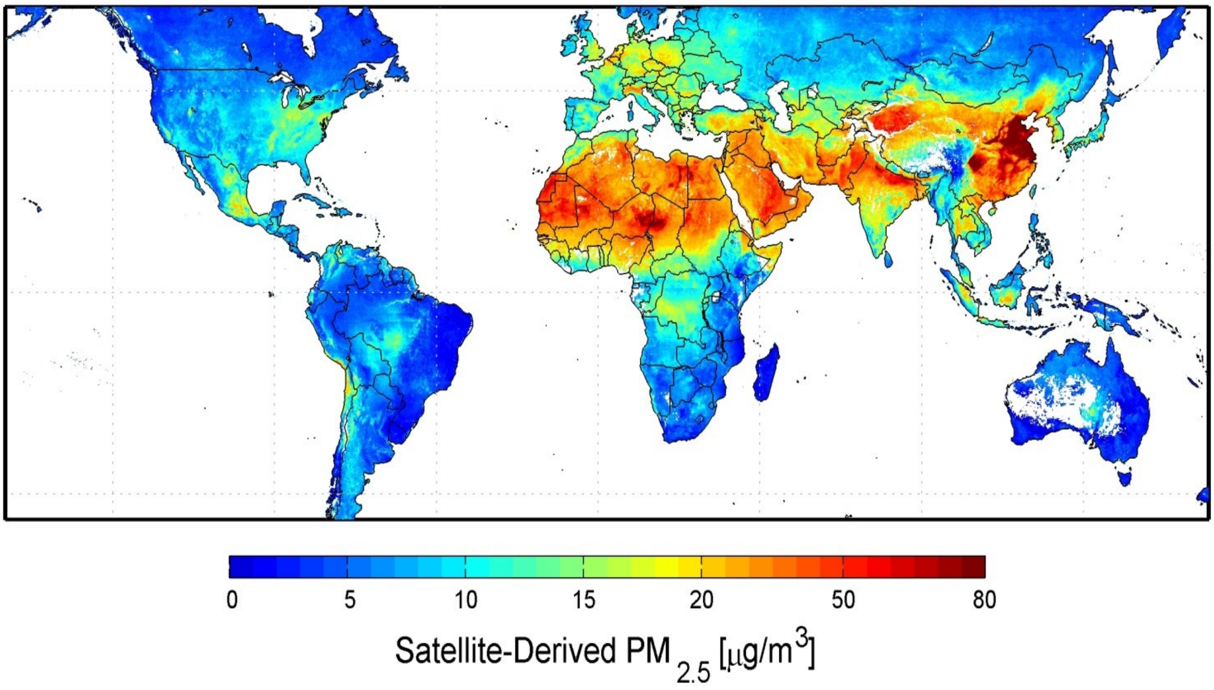


Figure 3. Global map of $PM_{2.5}$ distribution above ground (2001-2006), adapted from Donkelaar Av, 2010

In the European Union (EU) countries, PM_{10} levels in at least some cities are below the annual WHO air quality guideline (AQG) level of 20 μg/m^3. Almost 83% of the population of the cities for which PM data exist is exposed to, PM_{10} levels exceeding the AQG levels. Although this proportion remains high, it is an improvement compared to previous years, with average PM_{10} levels slowly decreasing in most countries in the last decade [3]. Emissions from road traffic and biomass burning are frequently reported to be the major causes. As a consequence of these exceedances a large number of air quality plans, most of them focusing on traffic emissions reductions, have been implemented in the last decade [57] (and references therein). The highest measured PM_{10} and $PM_{2.5}$ annual mean concentrations at rural background sites in 2011were in Italy and the Czech Republic, with annual means above the PM_{10} limit value of 40 µg/m^3 and the $PM_{2.5}$ target value of 25 µg/m^3 [58].

Particulate source composition is a dominant factor in the determination of spatial variability [49]. In the Netherland a study by Mooibroek et al., 2011 [59] was discussed the spatial variation of different sources of $PM_{2.5}$. The contributions of secondary inorganics to $PM_{2.5}$ were highest (46-48%) at the rural sites, whereas lower contributions were found at the urban sites in the Rotterdam area. Total carbon matter (TCM) showed lower contribution (26%) at rural stations, whereas the maximum (41%) was found at the curbside in Rotterdam illustrating the impact of traffic emissions. Spatial variability was also found for the residual oil combustion source, with higher source contributions at both of Rotterdam (curbside background) and Schiedam (urban site background) comparing to the other rural sites. It was referred to the nearby harbor activities, intensive shipping and petrochemical industries located in the Port of Rotterdam.

PM concentrations varied greatly between and within land use categories. Spatial characteristics of the sites background, such as elevation and distance from major roads, were found to be significant in predicting mass concentrations [47]. Significant spatial variability of PM_{10} concentrations between cities across Europe has been reported based upon routine monitoring data, a series of research projects and a wintertime study in 14 European cities. The lowest concentrations were generally found in Northern Europe and the highest in Southern and Eastern Europe. Spatial variation of $PM_{2.5}$ across Europe is less well characterized because it is not routinely measured in most monitoring networks. Nevertheless, significant northesouth gradients have been also reported for $PM_{2.5}$ [60] (and references therein). However, Reche et. al., 2011 [57] had reported in his study the average PM_{10} concentration at different sites in each of UK, Spain and Switzerland. For urban background sites, PM_{10} concentrations were found to be 18, 23 and 30 µg/m^3 at London (UK), Lugano (Switzerland) and Barcelona (Spain) respectively. While for traffic background sites, PM_{10} concentrations were found to be 27 µg/m^3 at Bern (Switzerland) and 32µg m^{-3} at London (UK). For the two sites in Spain, the PM_{10} concentrations were 21 µg/m^3 at Sta Cruz Tenerife (shipping background) and 23 µg/m^3 at Huelva (industrial background).

A better understanding of the contribution of factors, such as regional and long range transport of PM, local pollution sources or other processes, to the generation of elevated PM levels in urban areas is of great importance [21]. A study of spatial variability of PM_{10} and $PM_{2.5}$ at 4 different urban sites across Europe was performed by Lianou et. al., 2011 [61]. The mean of PM concentrations were found to be 15.4, 56.7, 31.1 and 21.8 µg/m^3 of PM_{10} and were 9.0, 25.0, 21.5 and 13.5 µg/m^3 of $PM_{2.5}$ in Helsinki, Athens, Amsterdam and Birmingham respectively. Higher levels of PM_{10} and $PM_{2.5}$ were detected in Athens as compared to the other cities. PM_{10} and $PM_{2.5}$ levels among the four urban areas were consistent with the spatial variation of PM in Europe, which is described by increasing PM from north-to-south and west-to-east. The differences for particle mass across the four urban areas in Europe indicated the important role of local sources and characteristics as well as variations in the inputs of local vs. regional sources. As a result, residents were exposed to different mixtures of particles causing different health responses. In addition, these trends have an impact on the ability of countries to comply with existing EU-wide directives and test the effectiveness of mitigation policies.

1.3.2 Temporal Variability

In Europe, generally higher concentrations of different PM fractions are observed during the winter season. The diurnal variation of mass concentrations of all fractions showed basically the two maxima in the morning and in the afternoon more pronounced in winter than in summer [62]. The secondary inorganic aerosol (SIA) and SOA contribution varies substantially across Europe and with season. The SIA contribution is higher in winter, due to increased emissions from combustion in the cold season, and the SOA contribution is generally higher in summer, when emissions from terrestrial vegetation are larger, increasing from the northern parts to the southern parts of the continent [58, 63].The differences in PM concentrations depending on a time of the day and sources were found as researchers analyzed diurnal particulate concentrations. An increase of primary pollutant concentrations is observed nights and early morning and it can be explained by residential wood combustion and heavy traffic. Since the mixing layer is deep during day hours primary particulate matter level is not high while concentrations of secondary particulate matter increase at noon where the sunlight creates conditions for photochemical reactions. Rapid increases in concentrations in early mornings are associated with local mobile sources and characterized by elementary (soot) and organic carbon [64] (and references therein).

1.4 Inorganic Aerosol Compounds

The chemical compositions of PM usually include sulfates, nitrates, ammonium, inorganic ions, elemental carbon (EC), organic carbon (OC), crustal material, particle-bound water and metals. These chemical species can provide an initial indication of the biogenic and/or anthropogenic origins of particles. A large part of the PM mass (25-75%) is inorganic, with sulfates, nitrates, ammonium, sodium and chloride being the dominant species (Fig.4). Sulfate, nitrate, ammonium and trace elements such as metals are the major components of fine PM mode. By contrast, coarse PM mode constituents are primarily crustal, consisting of Si, Ca, Al, Fe, and K (note that small amounts of Fe and K are also found among the fine PM but stem from different sources). Sodium, chloride in addition to the crustal components are mainly found in the coarse mode [1, 65]. A portion of inorganic PM is generally classified as “crustal material” or “dust” with Si, Al, Ca, K, Mg and Na being its major constituents. Mineral dust tends to originate from specific areas in the Earth and can be transported over very long distances, influencing climate and atmospheric chemistry on regional and global scales[65]. On the other hand, sea-salt is one of the major contributors to the mass of particulate matter emitted into the atmosphere globally[66]. In addition, sea-salt aerosol particles are carriers of species containing Cl, Br, I and S and therefore play a role in the atmospheric cycles of these important elements [67].

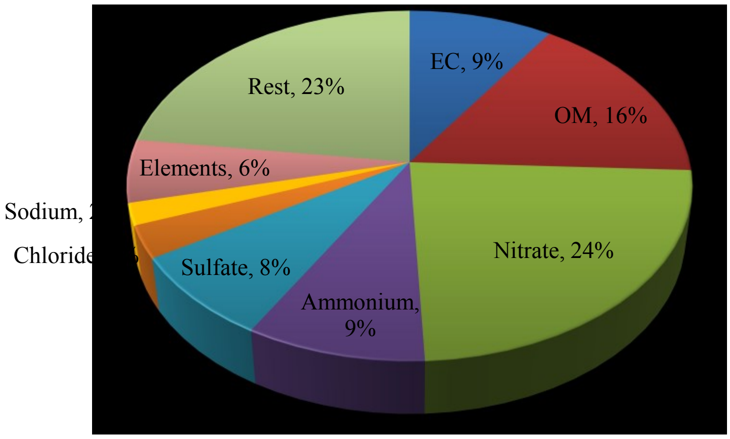


Figure 4. Average composition of PM_{10} collected during winter 2007/2008 at 6 sampling sites in Augsburg city, Germany

In the following the main inorganic aerosol compounds and their emission sources in the atmosphere are described.

1.4.1. Metal Oxides

Numerous natural processes release PM into the atmosphere. Typical of these processes are volcano eruptions and the blowing of dust and soil by the wind. The activities of man also release; for example, in the form of dust particles from construction, fly ash from smelters and mining operations and smoke from incomplete combustion processes. Metal oxides, which form a major class of inorganic particles in the atmosphere, are produced whenever fuels containing metals are burned. For example, during the combustion of pyrite-containing coal, particulate iron oxide is formed. Part of the calcium carbonate in the ash fraction of coal gets converted to calcium oxide, and goes to the atmosphere through the stack [68].

1.4.2. Sulfate

Sulfate is a major component of the atmospheric aerosol and drives the formation of new aerosol particles through nucleation. Sulfate is mainly produced within the atmosphere by oxidation of sulfur dioxide (SO_2), which is itself directly emitted (e.g. from fossil fuel combustion, industrial processes, and volcanoes) or produced within the atmosphere by oxidation of reduced sulfur species such as dimethyl sulfide (DMS) emitted by oceanic phytoplankton. The oxidation of SO_2 can take place in the gas phase and in the aqueous phase. However, deliquescent sea-salt and dust aerosols have also been suggested as important sites for aqueous phase sulfate production because of the rapid rate of SO_2 oxidation by ozone in alkaline solutions [69] (and references therein).

Coal combustion is one of the largest primary sources of sulfate in the atmosphere [70]. SO_2 is emitted from coal-fired power plants [71], and is the main contributors to secondary sulfate in Central Europe. Formation of sulfate is chemically linked to primary emissions of SO_2 and to the abundance of atmospheric oxidants such as hydroxyl radical (OH), hydrogen peroxide (H_2O_2), ozone (O_3), methylhydroperoxide (MHP), and peroxyacetic acid (PAA) [1]. All of these oxidant species are formed via photochemical reactions which originate from emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOC). Therefore, it is expected that variations in primary emissions of NO_x and VOC may have an effect on the amount and distribution of sulfate in atmosphere [72].

1.4.3. Nitrate and Ammonium

Combustion of fossil fuels, biofuels, and biomass besides lightning converts or “fixes” inert nitrogen gas (N_2) into a highly reactive form (NO_x) and are the main sources of nitrate and ammonia. Other emission sources of NO_x to the atmosphere include microbial processes in soils and transport from the stratosphere [73]. Anthropogenic activities currently dominate NO_x sources to the troposphere [74].

NO_x are emitted from combustion processes and is then present in the atmosphere in the form of gaseous NO and NO_2. NO is slowly transforming into NO_2 by reacting with oxygen in the atmosphere (this is why NO_2 is both a primary and a secondary component), and some of the NO_2 dry deposits close to the source. Some of the NO_2 and NO transforms into nitric acid (HNO_3) which subsequently transforms into NO_3^- in particulate form. As for ammonium the lifetime of particulate nitrate can be quite long and the most important removal pathway is also wet deposition. NH_3 is primarily emitted from processes related to agriculture such as livestock production (including the spread of manure) and fertilizer application and production. NH_3 emissions are therefore quite high in countries with widespread intense agricultural activities. Although that road traffic is a major source of NO_x but the increasing use of three-way catalysts on cars has led to increasing emissions of NH_3 from vehicle exhausts [75, 76]. Fig.5 illustrate of the path ways of reactive nitrogen in the atmosphere which adapted from Hertel et. al., 2011 [77].

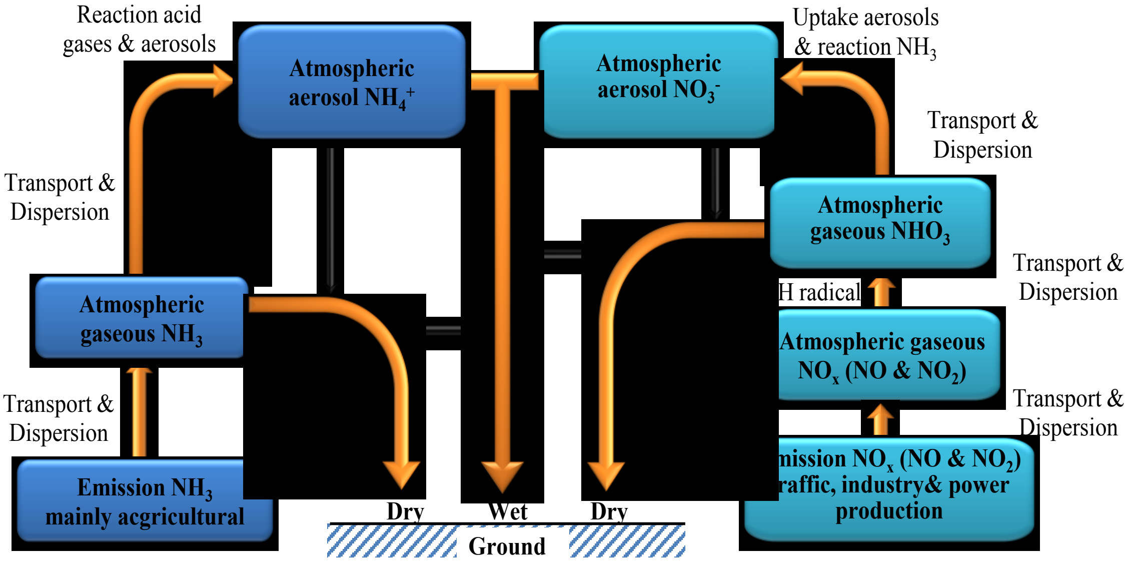


Figure 5. The pathways of reactive nitrogen in the atmosphere, adapted from Hertel et. al., 2011

1.4.4. Other Elements

All other individual inorganic species typically representing more than 1% of the total PM mass. Dust may be re-suspended in the atmosphere either by abrasion (when there is a disturbance on the surface like the passing of vehicle or the hopping motion of other particles, through a process known as saltation), or by means of the direct action of the wind on the surface. Additionally, other sources, like traffic, may affect the composition of deposited dust, which will be re-suspended later [78] (and references therein). Fe, Mn, K, Al, Ca, Ti and V these elements are mostly known as the composition of soil and road dust[79]. The dominant source of crustal elements such as Mg, Mn, Al, Si, Ca, Zr and Fe is fugitive dust which are include unpaved and paved roads, agricultural soil and construction dust [70]. K is also assumed to be a tracer for biomass burning [80] and it is dominated with Cl in major categories of biomass like wild fires, agricultural burning, residential wood combustion, prescribed burning for land management and wood-fired boilers[70]. In addition, the Cl, Br and S are inferred to sea-salt [81] considering that it was mainly distributed in the coarse size range. Elements such As, S, Sr, and Se are known as indicators of coal combustion [70, 82]. It is well known that diesel engines are the largest source of elemental carbon (EC) [83, 84] but they also emit large quantities of Zn [70]. Both V and Ni are known as the indicator of oil combustion [70, 85]. Cu, Zn, Ni, Pb and Se were found to be emitted from nonferrous metal sources in the atmosphere [20]. Unpaved road dust is the largest source of Pb. This may be due to the re-suspension of motor vehicle exhaust that deposited on road surfaces prior to banning of leaded fuel [86]. Industrial processing of copper is the largest source of Cu[70]. Surface coating operations emit the largest quantities of Ti, Sb, and La. While coal combustion is shown to be the largest source of Hg nationwide, wild fires also make a significant contribution [87]. A major portion of transition metals (Cu, Ba, Fe and Mn) [88] beside Antimony (Sb) [89] are released through abrasive vehicular emissions and have often been used as a tracer for dust from brake linings.

1.5 Carbonaceous Aerosol Compounds

Carbonaceous aerosols make up a significant fraction of particles in the atmosphere and include EC and OC, which are two important components of airborne PM. The importance is derived from their mass share of e.g. PM_{10} and $PM_{2.5}$, their property to absorb (EC) or scatter (EC and OC) light and their possible interference with human health [7]. EC (always in quotes) is conventionally and carelessly used in the literature, usually implying a near-elemental soot-carbon like composition, and in most cases referring to the fraction of carbon that is oxidized in combustion analysis above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere [90]. EC is black, often called “soot.” EC contains pure graphitic carbon, but it also contains high molecular weight, dark-colored and non-volatile organic materials such as tar, biogenics and coke [91] and could be defined technically as the residue of ambient samples after the extraction of OC fraction . EC occurs as the mineral graphite or as diamond in its purest forms, but these structures of more than 0.1 µg are seldom found in ambient PM [92]. EC is emitted mainly from combustion sources [93] and motor vehicle emissions [94, 95]. Freshly emitted diesel soot consists of agglomerates of small spherical graphitic particles consistent in size from 20 to 30 nm [92]. During combustion, elemental/black carbon (EC/BC) is released directly into the atmosphere [96]. Fuels are oxidized and pyrolyzed through the high temperature combustion processes into molecules, which are released into the atmosphere. Nuclei form and rapidly develop into larger compounds through particle surface reactions. These particles form chain-like aggregates resulting in visible particles up to several microns in size, chemically similar to impure graphite. Other carbon compounds included in this category are high molecular weight, non-volatile organic species [91].

Particulate organic carbon (OC) consists of thousands of organic compounds and comprise about 48–60% of the organic matter (OM) [97]. OC could be also defined technically as the extractable part of PM by either thermal desorption or solvent extraction. OC may be derived from direct, primary emission sources (e. g. residential heating and motor vehicles) as well as from gaseous precursors while EC can only originate from primary emission. Direct particulate OC emission may be from incomplete combustion, re-suspension of biological particles like spores, fungi, plant debris or abrasion products from tires and plastics. Similarly, anthropogenic and natural emissions also lead to particulate OC by the release of precursors (volatile organic carbon-VOC) and their subsequent distribution to particulate organic compounds (POC) [7] or it can be formed in the atmosphere through condensation of low-volatility oxidation products from volatile precursors (forming secondary organic aerosol - SOA) [92].

Recently, optical and thermal analysis experiments have provided strong evidence for the existence of a class of light absorbing OC. This substance, known as brown carbon (BrC) for its light brownish color, absorbs strongly in the ultraviolet wavelengths and less significantly going into the visible. Types of BrC include tar materials from smoldering fires or solid fuel combustion and pyrolysis products from biomass burning [98].

OC is more abundant than EC in emissions from low temperature combustion processes such as biomass burning [96].The relative proportion of these two species in emissions can indicate particle origin. Identifying sources contributing to emissions of this substance is difficult, due to its non-uniqueness. However, the proportion of OC to EC in emissions is considered indicative of source origin and is often used in this capacity. Table 1 shows the average of OC to EC ratios from different sources of emission as reported by Na et.al., 2004 [99] (and literatures therein). These different OC/EC ratios indicate that OC/EC ratios vary considerably from source to source due to different source emission strengths of OC and EC.

Table 1. Average of OC to EC ratios from different sources of emission adapted from Na et.al., 2004 and references therein.

Emission source	EC	OC	OC/EC ratio
Light-duty gasoline vehicles [a]	13.5	30.1	2.2
Heavy-duty diesel vehicles [a]	40.5	32.6	0.8
Paved road dust [b]	1.1	14.7	13.1
Residential wood combustion [b]	12.4	51.4	4.2
Natural gas home appliances [a]	6.7	84.9	12.7
Forest fire [a]	3.2	46.9	14.5

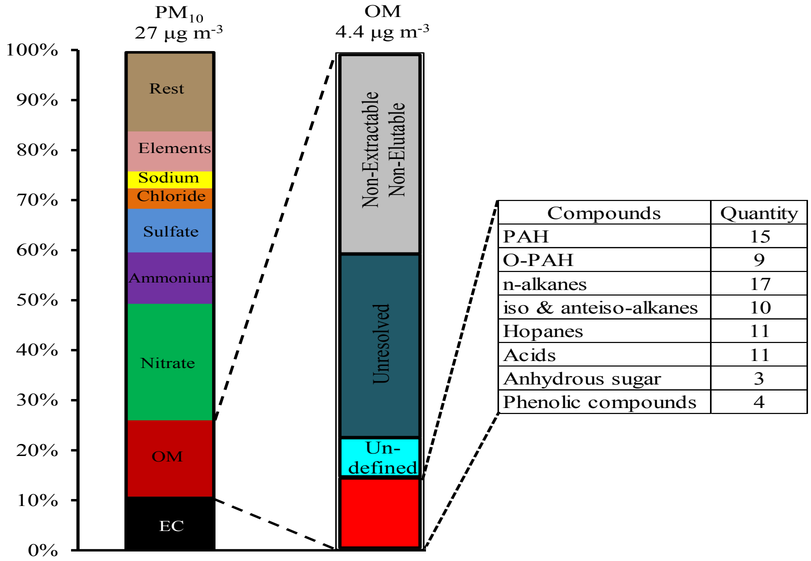
[a] Mass % of fine particle mass
[b] Mass concentration

Furthermore, the relative level of oxidation of the organic matter (OM) in the atmospheric aerosol has been used as an estimate of the degree of chemical processing in the atmosphere and represented as OM/OC ratio. The value of the OM/OC for ambient aerosols is subject to many factors, including the methodology in estimation. The OM/OC ratio for several published studies and suggested the use of values of 1.6 and 2.1 for OM/OC for urban and rural sites, respectively. While other studies have reported that the OM/OC values were found to be within the range from 1.2 to 1.6, with an average of 1.4 [100] (and references therein). The main classes of organic aerosol compounds and their emission sources in the atmosphere are described in details in the next chapter.

2. ORGANIC AEROSOL COMPOUNDS

2.1 Organic Matter

The organic constituents accounted up to 40% of total airborne PM mass and influence the behavior and impact of PM on human health, regional visibility and global climate. Much more complex is the composition of organic matter (OM) comparing to the inorganics as this class constitutes a relevant fraction of PM mass (20-60%) but includes a wide variety of individual species, mostly at very low concentration level and in general none of them individually constitutes more than 1% of the total mass; for this reason organic compounds are often considered as a whole (OM). OM can be measured as a whole, but only a small part of the species that constitute this group has been identified [101]. Fig.6 shows the average speciation of organic aerosol of PM_{10} samples from six sampling sites in Augsburg, Germany.



Compounds	Quantity
PAH	15
O-PAH	9
n-alkanes	17
iso & anteiso-alkanes	10
Hopanes	11
Acids	11
Anhydrous sugar	3
Phenolic compounds	4

Figure 6. Average speciation results for organic aerosol in Augsburg, Southern Germany for PM_{10} collected at 6 sampling sites. Even if about 80 of individual organic compounds are identified and quantified, they represent only 15 percent of the total organic mass.

The organic fraction of ambient particles is a complex mixture of thousands of organic compounds. These organic compounds are either emitted directly from sources (primary organic aerosol-POA) or can be formed by condensation of low-volatility oxidation products from volatile precursors (secondary organic aerosol-SOA formation) [102]. SOA contributions to OM vary with season and location but are typically substantial, 20-80% of measured mass of ambient $PM_{2.5}$ [103]. Major sources of the gaseous precursors for SOA are incomplete combustion (e. g. traffic, domestic heating and vegetation fires), biogenic emission (e. g. isoprene and terpenes) and VOC from industry (e. g. refineries, solvents and dry cleaners) [7]. As gaseous organic species are oxidized by species such as O_3, OH, or NO_3 radical, their reaction products accumulate. Some of these products have low volatilities and condense on available particles [102]. Mainly SOA is formed in the atmosphere due to photo-oxidation or nitration of precursor substances during the night [6]. Most SOA modeling has focused on the partitioning of organic products onto pre-existing nonacidic particles or by nucleation, leading to new particles. There is evidence to suggest that the interaction of sulfuric acid with atmospheric organics is expected to play an important role in the nucleation of new particles in the atmosphere [104]. The ability of a given volatile or semi volatile organic compound (VOC, SVOC) to produce SOA depends on four factors: its atmospheric abundance, its chemical reactivity, the availability of oxidants and the volatility of its products. Many VOC do not form PM under atmospheric conditions, owing to the high vapor pressure of their products [1]. The importance of emitted VOC as SOA precursors is quite variable, with many emitted compounds generally believed to be very inefficient at generating SOA. However, certain classes of VOC have long been identified as more likely to lead to SOA formation by virtue of their general high reactivity and types of oxidation product formed. Of particular significance are cyclic compounds, since the products of fragmentation (i.e., ring opening) processes often have the same (or similar) carbon number as the parent compound. Furthermore -in the cases of cycloalkenes- aromatic hydrocarbons and terpenes (the majority of which are cyclic), oxidation occurs predominantly by an addition mechanism, so that the first-generation products generally contain two (or more) polar functional groups. Consequently the oxidation of these classes of compounds is more likely to lead to the generation of low-volatility products than the oxidation of similar sized VOC in other classes. SOA precursors typically produce a large range of oxidation products, resulting in a considerable number of possible reaction pathways [104]. Carlton et. al., 2009 [103] had reviewed some of the pathways leading to SOA formation from isoprene as shown in Fig.7.

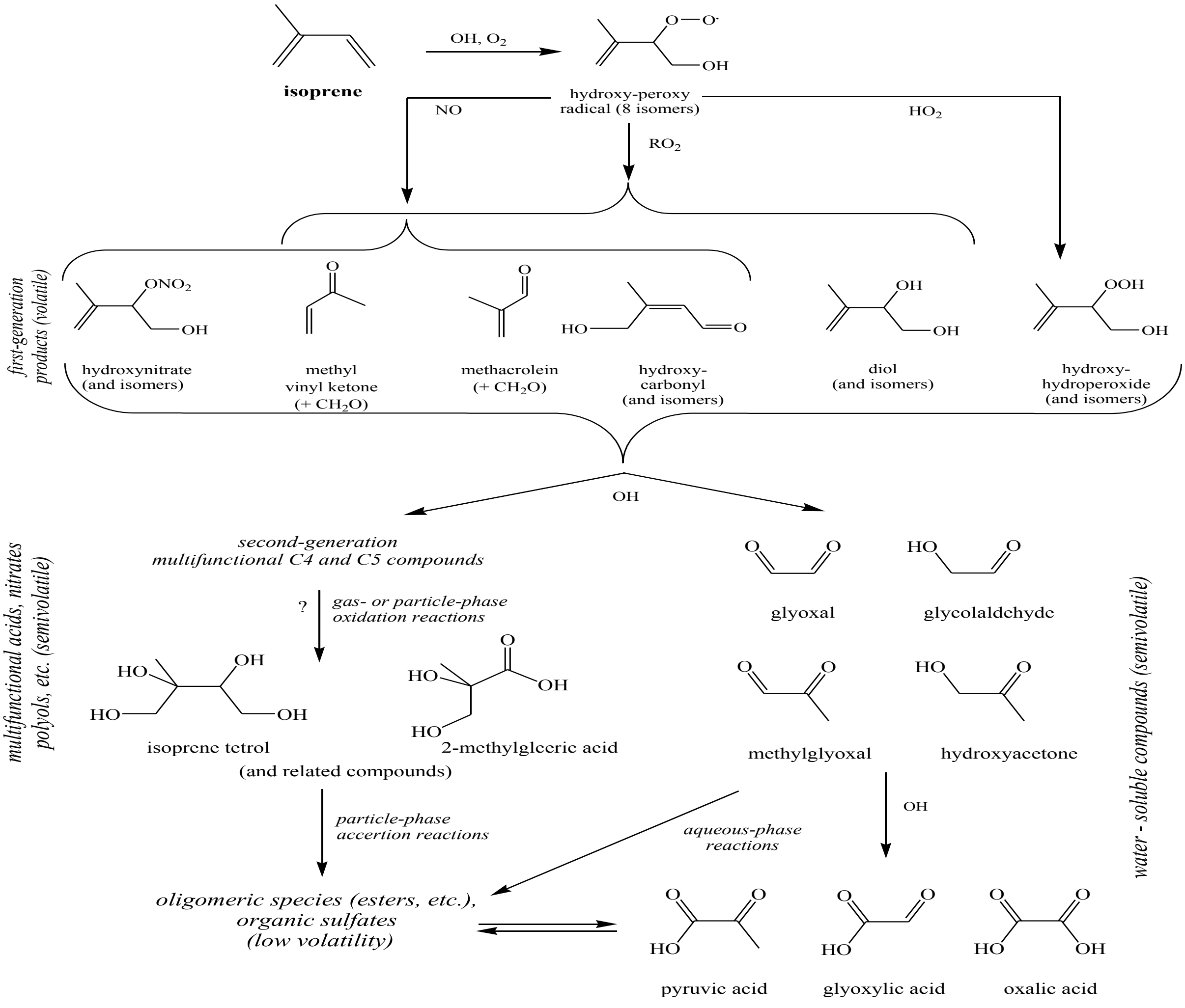


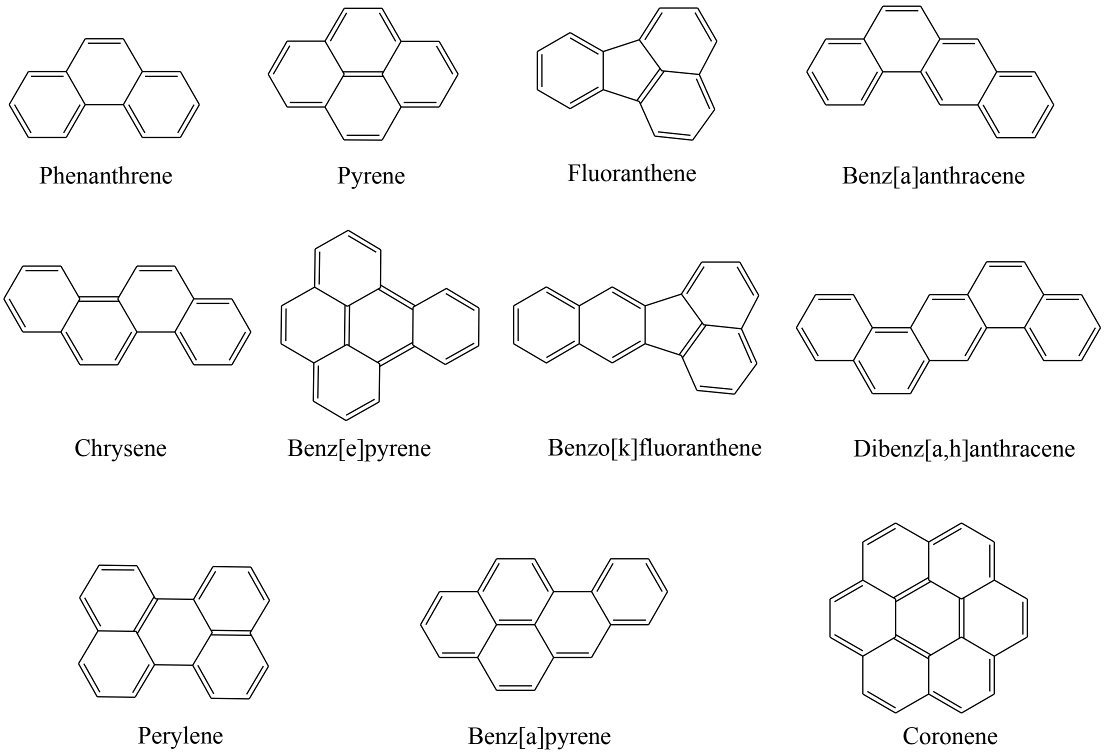
Figure 7. Oxidation pathways of isoprene leading to SOA formation. Adapted from Carlton et. al., 2009.

In the following, the main groups of particulate organic compounds (POC) and their emission sources in the atmosphere are described. The description is limited to those POC groups which have been analyzed in the ambient samples and were necessary for this work.

2.2 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic aromatic hydrocarbon (PAH) compounds are a class of complex organic chemicals, which include carbon and hydrogen with a fused ring structure containing at least 2 benzene rings. PAH may also contain additional fused rings that are not six-sided [105] and some representative structures of various PAH are shown in Fig.8. PAH are the most stable form of hydrocarbons having low hydrogen-to-carbon ratio and usually occur in complex mixtures rather than single compounds[105] (and references therein). In general, there are five major emission sources of PAH, i.e. domestic, mobile, industrial, agricultural and natural [106]. PAH are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood and from the release of petroleum products and spills. Other sources of PAH include oil seepage and diagenesis of organic matter in anoxic sediments [105] (and references therein). PAH are also found in tar vapors, tobacco smoke, barbecue smoke, as well as in oil consumption and automobile exhaust [105, 107-110].

Due to their low natural emission PAH are good tracers of anthropogenic sources of input to the atmosphere. In urban and near-city environments, the main PAH sources are vehicular emissions and domestic heating [111] with the contribution of the latter increasing significantly during winter [112] (and references therein). Some of the emission rates of PAH from various sources are listed in Table 2 that had been modified and adapted from Ravindra et. al., 2008 and references therein.



Phenanthrene Pyrene Fluoranthene Benz[a]anthracene

Chrysene Benz[e]pyrene Benzo[k]fluoranthene Dibenz[a,h]anthracene

Perylene Benz[a]pyrene Coronene

Figure 8. Chemical structure of some targeted PAH in ambient PM

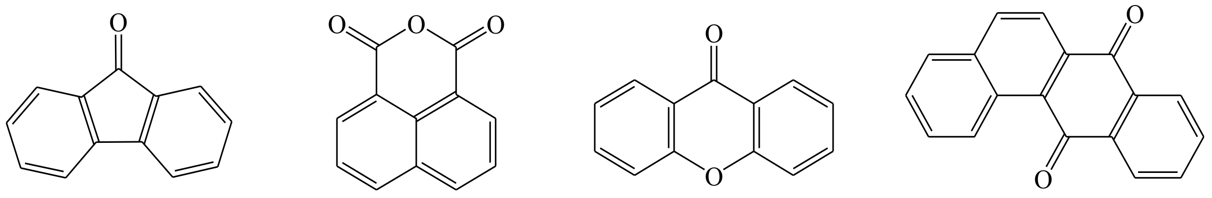
Table 2. Examples of estimated PAH emission rates from various sources modified and adapted from Ravindra et. al., 2008 and references therein.

PAH sources	Emission rate	Remarks
Domestic		
Natural gas home appliances	1–2000 pg kg^{-1}	pg/kg of natural gas burned.
Coal	0.95 mg kg^{-1}	Average of 4 coal ranks.
Wood	2.0–3.2 mg kg^{-1}	Wood combustion.
Mobile		
Gasoline engine	72.5 μg kg^{-1}	Light-duty vehicles.
Diesel engine	60.2 μg km^{-1}	Heavy-duty trucks.
Aircrafts	1.24 mg	Per landing-take off cycle for B[a]P.
Helicopter	63.4 mg l^{-1} Fuel	22 PAH.
Ships	500 μg kg^{-1}	Marine diesel engine, sum of 25 PAH.
Break dust	16 mg kg^{-1}	Emitted from the hydraulic break system.
Agricultural		
Open burning	5–683 mg kg^{-1}	Wind tunnel simulations of agricultural and forest biomass fuels burning.

There are many other anthropogenic sources of pyrolytic PAH. In fact, any industrial or domestic process in which organic carbon is subjected to high temperature will result in the production of some PAH [113].

2.3 Oxidized Polycyclic Aromatic Hydrocarbons (O-PAH)

Oxidized polycyclic aromatic hydrocarbons (O-PAH) are the products of incomplete combustion. O-PAH have been identified in source samples from gasoline, diesel, coal, wood, and municipal waste combustion. Photo oxidation of PAH has also been found to produce O-PAH from the oxidation of the PAH derived from combustion processes [114-117]. Solid fuel combustion using coal emits a large amount of carbonaceous aerosol containing organic constituents such as PAH and O-PAH [107]. PAH and O-PAH are also well associated with biomass combustion [18]. Some representative structures of various O-PAH are shown in Fig.9.



9H-Fluoren-9-one

1,8-Naphthalic anhydride

Xanthon

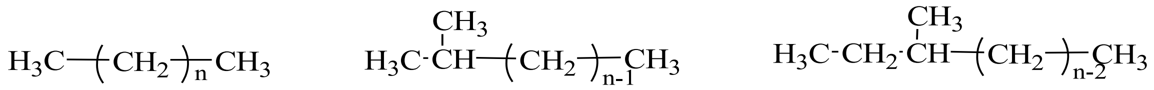
Benz[a]anthracene-7,12-dione

Figure 9. Chemical structure of some targeted O-PAH in ambient PM

2.4 Alkanes

The n-alkanes are an important class of organic compounds in ambient aerosols and their homologue distribution may indicate different pollution sources [118]. Anthropogenic sources typically include the combustion of fossil fuels, wood and agricultural debris or leaves. Biogenic sources include particles shed from the epicuticular waxes of vascular plants and from direct suspension of pollen, microorganisms (e.g., bacteria, fungi and fungal spores) and insects [23]. In the literature, higher plant waxes has been recorded as the source of long chain n-alkanes in aerosol samples [119, 120], while n-alkanes with a chain length around C_{20} mostly originate from unburned fuel [121]. An n-alkanes profile C_{max} (most abundant) $\geq C_{27}$ indicates inputs arising from higher plant waxes. A C_{max} between C_{23} and C_{25} serves as a marker for diesel exhaust [122] but they are only in relatively low concentrations in the fuels [117], whereas relatively high concentrations of these n-alkanes could derive from emissions of unburnt emitted lubricating oils [117, 123, 124]. The carbon preference index (CPI), defined as the ratio of the concentration of odd- to even-carbon numbered n-alkanes [125], has been widely used to evaluate biogenic and anthropogenic contributions to organic aerosols. Urban environments, with large contributions from anthropogenic emissions(fossil fuels), generally exhibit CPIs ranging between 1.1 and 2.0, while rural environments with larger biogenic impacts generally exhibit CPIs above 2.0 [126].

Iso- and anteiso-alkanes (C_{29}-C_{34}) are enriched in cigarette smoke particles showing a concentration pattern characteristic of tobacco leaf surface waxes that is distinctly different from leaf surface abrasion products shed from plant leaves. Relative to major leaf surface wax n-alkanes, these iso- and anteiso-alkanes are enriched by a factor of more than 40 in tobacco and tobacco smoke particles as compared to leaf surface waxes from other plants. It was found that the iso- and anteiso-alkanes concentration pattern generated by cigarette smoke is preserved in the urban atmosphere and is measured at levels that are comparable to emissions estimates based on daily cigarette consumption [127]. Fig.10 shows the bone structures of n-alkane, iso- and anteiso-alkane.



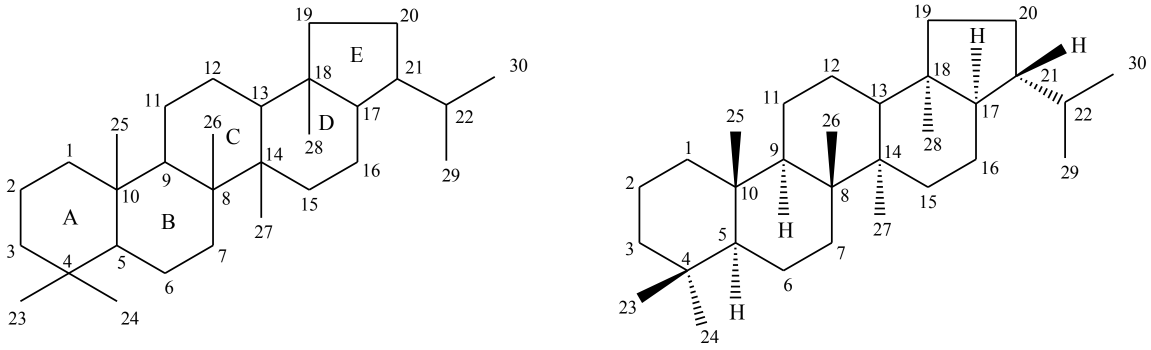
$H_3C-(CH_2)_n-CH_3$ $\quad$ $H_3C\text{-}\overset{CH_3}{\overset{|}{C}}H-(CH_2)_{n-1}-CH_3$ $\quad$ $H_3C\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}H-(CH_2)_{n-2}-CH_3$

n-alkane *iso*-alkane *anteiso*-alkane

Figure 10. Chemical bone structure of alkanes

2.5 Hopanes

Hopanes are of great importance as biomarkers in geochemistry due to their diversity. Fossil fuels such as coal and crude oil are the products of biogenic organic matter transformed in sedimentary deposits by diagenesis and catagenesis over millions of years [128]. Hopanes are formed during a process requiring geological times and probably the elevated temperatures reached during deep sediment burial. The functional groups and some or all carbon atoms of the side chain are lost. In modern sediments, the amounts of hopanes are small and masked by hopanes derived from contamination by fossil fuels, which confirms that the hopanes are an old material suitable for the confirmation of a mineral origin. Besides the steranes, the hopanes are the major biomarkers used for the characterization of petroleum. First, their carbon skeletons are related to their biogenic precursors and, therefore, to the source of the petroleum [129]. Second, the configurations at the positions C-17 and C-21 enable one to determine the maturity of an oil [130]. Finally, advanced biodegradation can be detected through the composition of the hopanes, since the various components degrade at different rates [131]. Sterane and triterpanoid hopanes have been identified in lubricating oils, vehicular exhaust, road dust, tire wear, roofing tar pot fumes and airborne suspended particles [128]. Fig.11 shows the characteristic structures of hopane and 17α(H), 21β(H)-hopane (30ab) as example. Hopanes are constituents of all mineral oil- or coal-based fuels and lubricants [132], and have been identified in emissions from coal burning [130], heating oil burning, and vehicles [128]. It has been confirmed that hopanes found in automobile exhausts are not from gasoline and diesel fuel, but from lubricating oil based on the similarity of hopanes distributions [133].



Hopane characteristic structure

17α (H), 21β(H)–Hopane (30ab)

Figure 11. Hopane characteristic structures. The 17α(H), 21β(H)-hopane (30ab) as example for detected hopanes in PM

The homohopane index (31abs/31abs+31abR) [18] for coal combustion aerosols increases with increasing coal maturity [134] but is higher in mineral oil-based sources. The homohopane index found in emissions from coal combustion ranges from approximately 0.1 for lignite coal to approximately 0.4 for bituminous coal, and ranges from 0.54-0.67 for vehicular emissions and fuel oil consumption [18].

2.6 Anhydrous Sugars

Biomass burning is a primary source which emits high amounts of organic aerosol (OA) and can largely contribute to the organic carbon (OC) mass of PM in winter [135]. Among the large indefinite numbers of molecular compounds emitted by biomass burning, the three isomeric monosaccharide anhydrides (MA) (anhydrous sugars) levoglucosan (1,6-anhydro-β-D-glucopyranose), Mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) formed during pyrolysis of cellulose and hemicellulose are the predominant organic compounds (Fig. 8) [111]. Due to their low vapor pressures, MA are in the atmosphere in particulate phase. Especially levoglucosan, because relative kinetics indicates that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when wood combustion particles are exposed to 1 × 10^6 molecules cm^{-3} of OH (typical average summertime conditions). This implies that levoglucosan reacts with OH on a timescale similar to that of transport and deposition, which has important implications for the use of levoglucosan as a tracer for biomass burning emissions in source apportionment studies[136]. However, the degradation of levoglucosan by atmospheric free radicals is possible and could potentially affect its atmospheric concentrations. The aqueous oxidation of levoglucosan by OH radical to form higher molecular weight compounds (HMWCs) was reported. It was found that the mean degradation fluxes of levoglucosan (oxidized by OH radical) during daytime was found to be about 7.2 ng m^{-3} h^{-1} in summer and 4.7 ng m^{-3} h^{-1} in winter [137] (and references therein). Lower degradation fluxes of levoglucosan in winter is referred to the lower concentration of OH radical in winter due to the low intensity of solar radiation and thus the low photochemical reactivity [138].

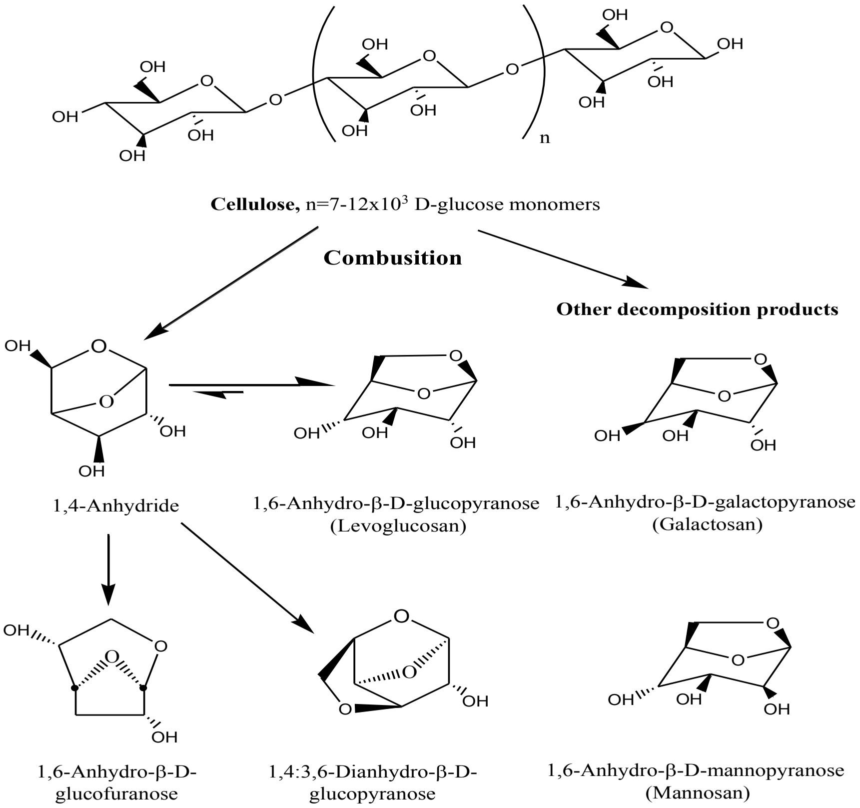
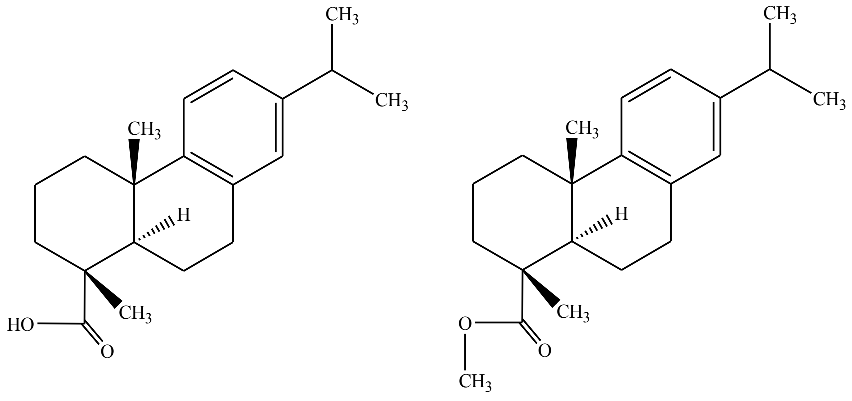


Figure 12. The major decomposition products from burning of cellulose. Levoglucosan is the dominant compound, mannosan and galactosan are formed as well as levoglucosan from burning of hemicelluloses.

2.7 Resin Acids

Resin acids, which are biosynthesized mainly by gymnosperms (e.g. pine and spruce) in temperate regions [139, 140], are generally found in aerosols in significant concentrations. They include unaltered (levopimaric, pimaric, isopimaric and sandaracopimaric acids) and thermal degradation products (neoabietic, palustric, dehydroabietic and 7-oxodehydroabietic acids) [139]. Resin acids are also tracers for biomass burning [141], with the most abundant detected being dehydroabietic acid (DHA) and dehydroabietic acid methyl ester(DHA-ME) (Fig.13). DHA acid signal often exhibits a strong correlation with the measured ambient PM concentrations due to its presence in both plant residues and car tires [142]. DHA has been used as a biogenic source indicator for conifer resin, either directly to the aerosol, or from combustion of wood [143]. Recently, DHA has been suggested as a marker for wood smoke. Unlike levoglucosan, which can be used to trace all wood combustion, DHA is found solely in emissions from burning of coniferous wood and therefore can be used to distinguish coniferous wood from hardwood combustion [22]. DHA is also constituent of vehicle tires, indicating another possible source [144].



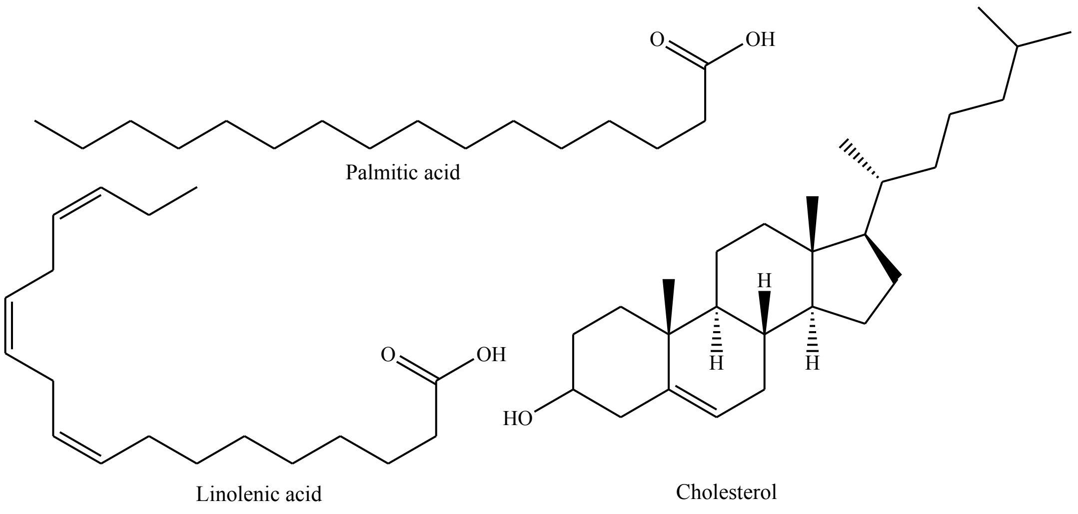
Dehydroabietic acid

Dehydroabietic acid methyl ester

Figure 13. Resin acids, dehydroabietic acid (DHA) and dehydroabietic acid methyl ester (DHA-ME)

2.8 Fatty Acids and Cholesterol

All fatty acids between C_{10} and C_{26} with palmitic acid as the major saturated component and linolenic acid as the major unsaturated component (Fig.14), have been reported to be present in tobacco smoke [145]. Food cooking has been shown to be an important source of the fine organic aerosol in urban environments [146]. Cooking emissions was reported as another source for fatty acids and cholesterol [94]. Cholesterol is a known tracer molecule for meat cooking emissions [14].



Palmitic acid

Linolenic acid

Cholesterol

Figure 14. Chemical structure of palmatic acid, linolenic acid and cholesterol

2.9 Phenolic Compounds

Combustion of wood and other biomass fuels produces source specific organic compounds arising from pyrolysis of lignin, including substantial amounts of 4-substituted methoxylated phenolic compounds, which, as it occurs with anhydrous sugars or resin acids, have been used as atmospheric markers to determine the contribution of wood smoke to ambient atmospheric fine particulate matter [147]. Gymnosperm smoke is made up almost exclusively from 4-hydroxy-3-methoxy-phenyl (guaiacyl or vanillyl) compounds. Angiosperms generate both vanillyl and 4-hydroxy-3,5-dimethoxyphenyl (syringyl) constituents [148]. Phenolic compounds such as acetosyringone, syringylacetone and syringic acid are considered as molecular markers for hardwood smoke [94, 149]. Syringyl compounds derived from sinapyl alcohol are generally more abundant in the hard wood smokes than their guaiacyl analogues derived from coniferyl alcohol (Fig.15), though lesser amounts of these are also present [149].

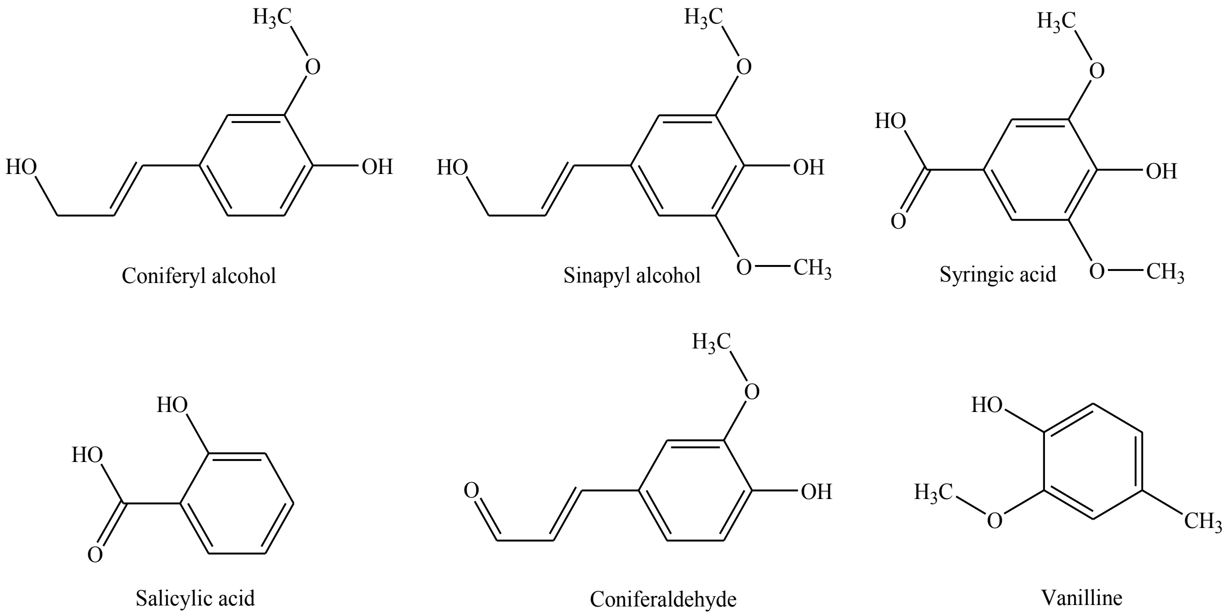


Figure 15. Examples of Phenolic compounds derived from sinapyl and coniferyl alcohol

3. SOURCE APPORTIONMENT

3.1. Introduction to Source Apportionment

Source apportionment (SA) of PM is important to identify the sources that are responsible for the ambient concentrations observed in a particular area. In the field of atmospheric sciences, SA models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants [150]. PM samples could be analyzed for their chemical composition, which identifies key species or groups of species that provide markers or tracers of sources. The organic portion of PM is the most difficult to characterize because it comprises a large number of compounds. However, it also holds the most promise in providing tracer compounds that are unique to individual sources and which can be used to accurately identify a source's contribution to the particulate matter problem. All of this information is important and necessary for development of effective and informed control strategies for particulate matter and toxic compounds. In a review of SA methods, Viana et al., 2008 (and references within) had reported that there are three main groups of SA techniques:

(I) Methods based on the evaluation of monitoring data. Basic numerical data treatment is used to identify sources. Examples are:

1- Correlation of wind direction with levels of measured components to identify source locations.
2- The correlation of gaseous pollutants with PM components to identify source associations.
3- Subtraction of levels measured at regional background from those obtained at urban background and/or roadside levels to identify the contributions from the regional background, the city background and the monitored street.
4- Quantification of natural PM contributions (e.g., African dust) by subtracting PM levels at regional background sites from those at urban background locations for specific days.

The main advantage is the simplicity of the methods and the consequent low impact of mathematical artefacts due to data treatment.

(II) Methods based on emission inventories and/or dispersion models to simulate aerosol emission, formation, transport and deposition. These models require detailed emission inventories that are not always available and they are limited by the accuracy of emission inventories, especially when natural emissions are important. A significant advantage of these methods is that they may be used in scenario studies to evaluate the impact of emission abatement strategies on the anthropogenic contribution to ambient PM concentrations.

(III) Methods based on the statistical evaluation of PM chemical data acquired at receptor sites (receptor models).

3.2. Receptor Models

Receptor models provide assessment of contributions from various sources based on observations at sampling sites (the "receptors") which increase the reliability of source apportionment [151]. The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. The main objective of receptor models is to identify the possible sources of PM and to obtain data on their contributions to the bulk PM mass [150]. An overview of the wide range of statistical models and modelling approaches which are currently available in the literature is shown in Fig.16 [152]. As shown in the graph, one of the main differences between models is the degree of knowledge required about the pollution sources prior to the application of receptor models.

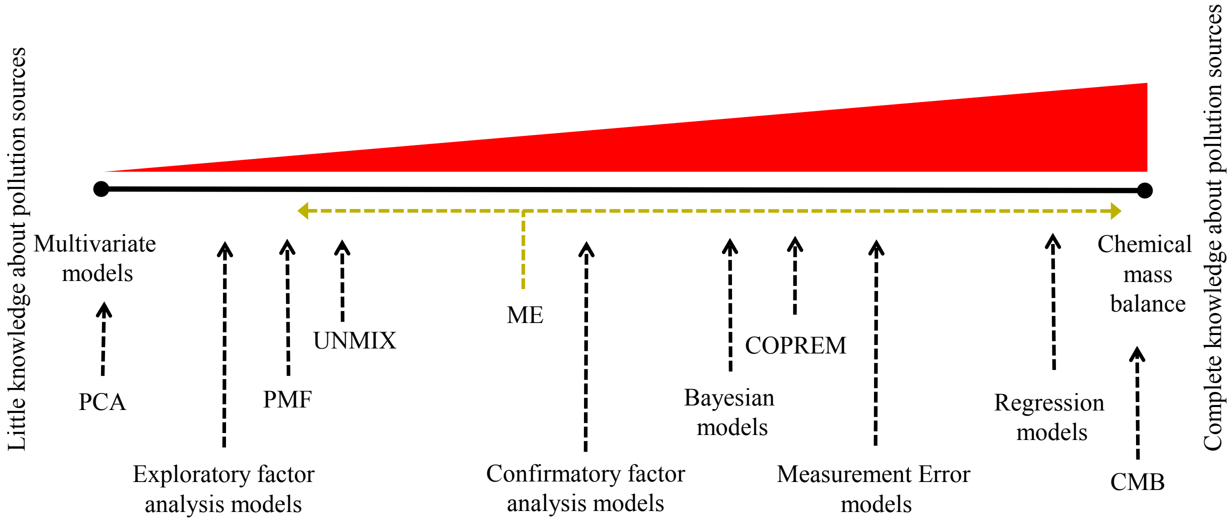


Figure 16. Approaches for using receptor models adapted and modified from Schauer et al., 2006. The full names of the receptor models can be found in the list of abbreviations.

The two main extremes of receptor models are chemical mass balance (CMB) and multivariate models. The CMB model assumes knowledge of the composition of the emissions for all relevant sources[153]. If changes of the source profiles between the emitter and the receptor may be considered minimal, CMB can be regarded as the ideal receptor model. However, these requirements are almost never completely fulfilled and thus, pure CMB approaches are often problematic. One important characteristic of CMB is that secondary aerosols must be included not as components of emission source profiles but as specific, single chemical compounds. This absence of mixture with other tracer elements is often regarded as a limitation and may lead to misinterpretation of results[150]. Multivariate receptor models (e.g., principal component analysis-PCA, positive matrix factorization-PMF, UNMIX) are based on the analysis of the correlation between measured concentrations. These types of receptor models are widely used because detailed prior knowledge of the sources and source profiles are not required. The assumption is that highly correlated compounds come from the same source and the chemical characteristics of the sources are constant throughout the measurement period [154].

3.3. Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices - factor contributions and factor profiles - which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis and emission inventories [155]. PMF is an advanced factor analysis technique based on a weighted least-squares fit and error estimates of the measured data. It was developed by Paatero [156, 157] and was employed to resolve dominant positive factors on the basis of observation without detailed prior knowledge of the sources and source profiles. A speciated data set can be viewed as a data matrix X of *i* by *j* dimensions, in which *i* number of samples and *j* chemical species were measured. The goal of multivariate receptor modeling is to identify the number of factors *p*, the species profile *f* of each source and the amount of mass *g* contributed by each factor to each individual sample (Equation 3.1):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad \text{….(3.1)}$$

where e_{ij} is the residual for each sample/species.

In PMF results are constrained so that no sample can have significantly negative source contributions. PMF uses both sample concentration and user provided uncertainty data to weight individual points. The PMF solution minimizes the object function *Q* (Equation 3.2), based upon these uncertainties (*u*).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \rightarrow Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{e_{ij}}{u_{ij}} \right]^2 \qquad \text{….(3.2)}$$

where e_{ij} represents the model uncertainties and u_{ij} the measured uncertainties. The uncertainty and stability of the solution is estimated by bootstrapping.

PMF results depend on the number of factors included in the model and the amount of rotation imposed on the solution. Interpretability of results is the key basis for judging the optimum values for these parameters. Interpretable solutions are those that grouped source-class-specific sets of markers into distinct factors. Models that grouped markers for multiple source classes into the same factor, distributed markers for one source class across multiple factors or contained factors with no distinctive groupings of compounds were judged less interpretable and rejected. While no molecular marker pattern can be unambiguously associated with a specific source class, this approach provides a systematic basis for sorting through the possible PMF model results [94]. More than 40% of the

European SA studies for PM have applied PMF and 7% some other type of factor analysis without non-negative constraints [158]. Many recent studies were carried out in Europe applying PMF for different fractions of PM with various time resolutions [16, 19, 59, 159-177].

4. ANALYTICAL METHODS

Within the scope of this work the selection of briefly described analytical methods is limited to those which were necessary for this work.

4.1. Gravimetric Analysis

Gravimetric analysis involves the measurement of net PM mass collected on a filter. The filter is weighed prior to and following sampling in a temperature and humidity-controlled environment. Filters are conditioned over a 24-hour period to minimize particulate volatilization and moisture bias and weighing is conducted using a micro-balance with sufficient sensitivity [91].

4.2. Ion Chromatography (IC)

Ion Chromatography (IC) is a common technique used to measure water-soluble (or inorganic) ions [178]. The water soluble components of PM such as Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, $Ca^{2+}$and Mg^{2+} are extracted from each sample using de-ionized water. The sample is injected into an eluent that passes through an ion exchange column. The ions are separated by the column, which uses a conductivity detector to quantify individual species. After passing through the ion exchange column, the sample enters a suppressor column where the chemical composition of one element is altered, producing a matrix of low conductivity. The ions are identified by the retention time and quantified by the conductivity peak area[91].

4.3. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Development of inductively coupled plasma (ICP) [179] and coupling with mass spectrometry (MS) has resulted in increasing acceptance in environmental applications, especially for the determination of rare-earth elements in soils and sediments and trace elements from filter substrates [180]. ICP-MS technique has a variety of characteristics that make it uniquely suited for the solution of chemical analysis problems in many applications [181]. Ion species generated from ICP and from the sample matrix can produce a significant background at certain masses, resulting in formation of polyatomic ions that can limit the ability of ICP-MS to determine some elements of interest. Cool plasma techniques have shown potential to detect elements at the ultra-trace level and to minimize common molecular ion interferences [182].

4.4. Analysis of Elemental and Organic Carbon

4.4.1 Thermal /Optical Analysis Method of EC and OC

Thermal/Optical methods are the most widely used and accepted approaches for aerosol EC and OC analysis [92, 183-185]. The methods are based on that low-volatility EC is not liberated in an inert atmosphere under temperatures <350°C; this allows the more volatile organic carbon (OC) to be separated from EC. Typically two phases of heating are implemented on aerosol particles collected on filters. First, OC evolves in inert atmosphere, where pyrolysis may occur. Since pyrolyzed organic carbon (PyOC) is artificial EC created in the measurement process, a laser is used to monitor the PyOC formation through the decrease of sample reflectance or transmittance to perform an "optical correction". The second phase involves heating in an oxidizing atmosphere in which both EC and PyOC are combusted. An organic pyrolysis (OP) fraction is defined as the carbon that evolves after the introduction of oxygen and before the laser signal (reflectance or transmittance) returns to its initial value (i.e., the crossover or split point). EC is quantified as the carbon evolved from the second phase minus OP [183].

In the following, the thermal optical method with the IMPROVE-A temperature protocol is briefly described. Particles collected on quartz fiber filters were heated within an inert atmosphere of He gas (>99.99%) by stepwise temperature program of 140, 280, 480 and 580 °C to determine OC. The carbon content is measured by transforming the desorbed carbonaceous species to carbon dioxide or methane with following detection by infrared spectroscopy (IR) or flame ionization detectors (FID). After the first step oxygen (2%) is added to the inert gas to oxidize the elemental carbon to carbon dioxide within a temperature program including steps at 580, 740 and 840 °C. Thereby the EC value is determined. The IMPROVE-A temperature protocol uses a laser thermal/optical reflectance (TOR) - Fig.17- or transmittance (TOT) method for the correction of EC/OC values [186-188]. The pyrolysis and charring of organic species on the filter during determination of OC could add elemental carbon to the original EC that was collected from the atmosphere [6].

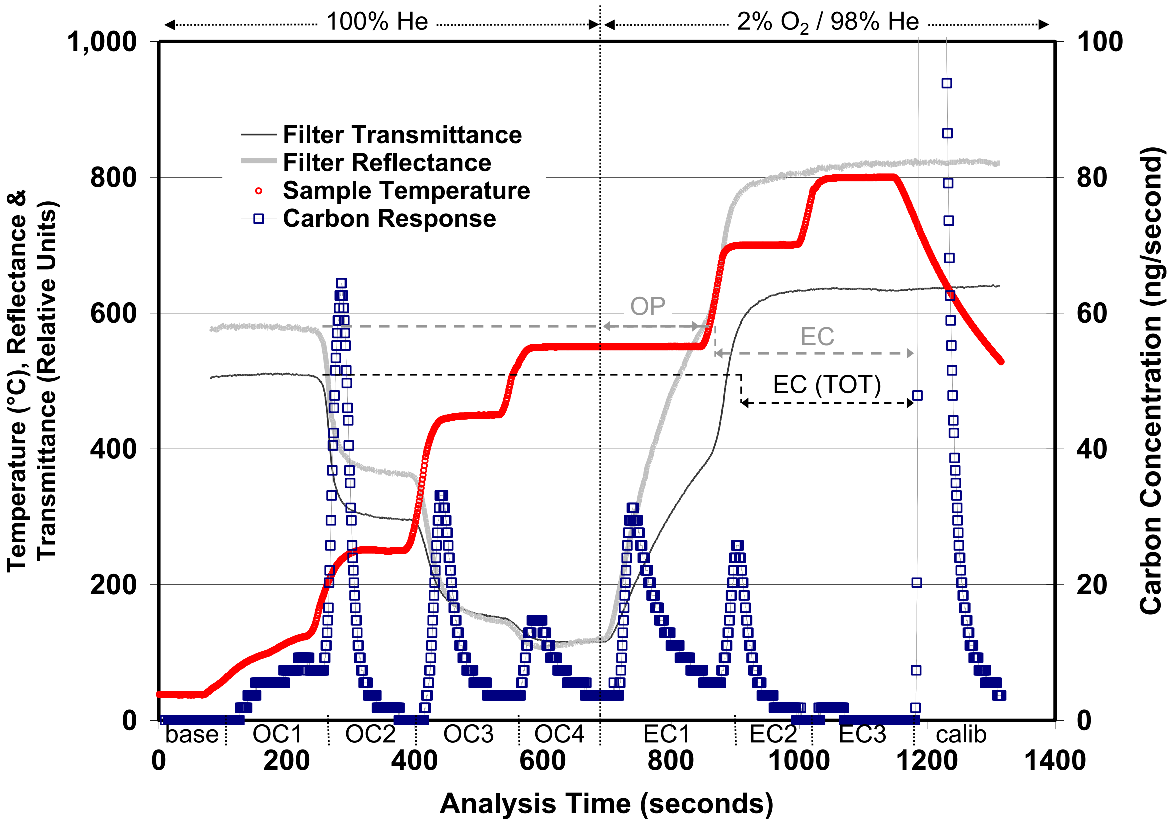


Figure 17. Example adapted from chow et. al., 2005, of an IMPROVE (TOR) carbon thermogram. Seven carbon fractions are defined by the analysis atmosphere and the sample temperature. OC1, OC2, OC3, and OC4 evolve in non-oxidizing pure helium (He) atmosphere while EC1, EC2, and EC3 evolve in 2% oxygen (O_2) and 98% He mixture. Optical charring corrections are determined by both reflectance (R) and transmittance (T) when these achieve their original values after O_2 is added.

4.4.2 VDI 2465 Analysis Method of EC and OC

In Germany, VDI 2465 Part 1 is a method involving extraction of OC by toluene and 2-propanol, thermo-desorption in a nitrogen flow and subsequent combustion has been established a standardized technique in addition to the thermal method. The VDI 2465 part 1 method include the solvent extraction of sample filter in a 1:1 mixture of toluene and 2-propanol for 24 h at room temperature for the removal of the extractable organic carbon from the ambient aerosol sample. After drying the filter for 4 h in a nitrogen stream, followed by 24 h in vacuum, the non-extractable organic carbon is removed by thermo-desorption in a nitrogen flow for 1 min at 200°C and 7 min at 500°C. The remaining carbon on the filter is then assigned to be EC. This fraction is combusted in an oxidizing atmosphere at 650°C and the emerging CO_2 is determined by coulometry [189].

4.5. Analysis of Organic Compounds by In situ Direct Thermal Desorption Gas Chromatography Time of Flight Mass Spectrometry (IDTD-GC-ToF-MS)

The in-situ derivatization thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS) was developed by Orasche et. al., 2011 for the determination of polar organic compounds together with non-polar compounds in one measurement [190]. Hydroxyl and carboxyl groups of compounds such as anhydrous sugars, alcohols and phenols, fatty acids and resin acids are targets of the derivatization procedure. Derivatization is based on silylation with N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) during the step of thermal desorption. The high temperature of 300°C during desorption is utilized for the in-situ derivatization on the collection substrate (quartz fiber filters) which accelerates the reaction rate. This implies that the analysis time is as short as it would have been without derivatization. For analysis, the filter surface is dampened with the derivatization reagent before insertion of the sample into the thermal desorption unit. To ensure ongoing derivatization during thermal desorption the carrier gas is enriched with MSTFA until the desorption procedure is finished (Fig.18). The analytical precision of all studied analytes were below 17% within a calibration range (total amount) from 22 pg for abietic acid up to 342 ng for levoglucosan. Limits of quantification (LOQ) for PAH were between 1pg for fluoranthene and 8 pg for indeno[1,2,3-cd]pyrene, for resin acids 37-102 pg and for studied phenols 4-144 pg. LOQ for levoglucosan was 17 pg. A positive side effect demonstrated is the minimization of matrix effects by deactivation of active quartz surfaces caused by the use of MSTFA during thermal desorption. An improvement of LOD/LOQ for PAH was shown and can also be expected for further analytes. It is strictly recommended to employ a large set of isotope-labelled standards. The advantages of isotope-labeled internal standards in GC-MS are well known. They gain an even higher importance for thermal desorption methods. The response of organic compounds depends on the composition of the particle matrix and on the quartz fibers. When compared to solvent extraction, not only does a fraction of this matrix affect the analysis but the whole sample composition. This fact should always be kept in mind when applying thermal desorption techniques [6].

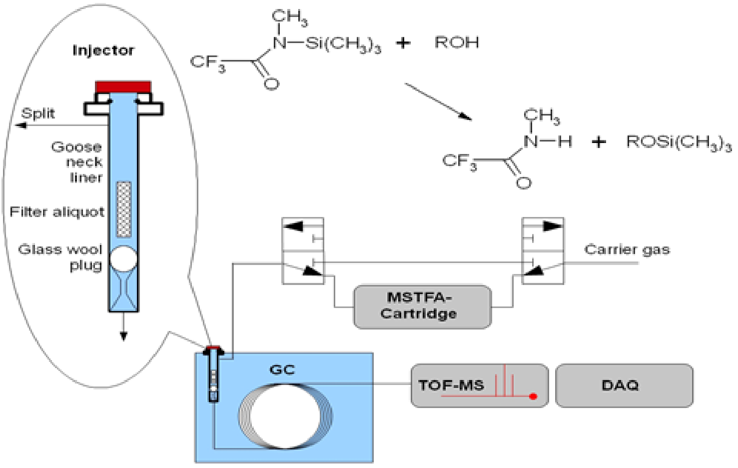


Figure 18. In-situ deri [illegible] figure: chemical equation of the silylation reaction of polar organic compounds with MSTFA.

5. RESULTS

In this chapter, the following sections will introduce the results which have been published in three publications. A detailed discussion and description can be found in the published papers (Qadir et al., 2014 and 2013). The data present in section 5.3 are from manuscript accepted for publication by Environmental Pollution journal.

5.1. Spatial and temporal variability of source contributions to ambient PM_{10} during winter in Augsburg, Germany using organic and inorganic tracers

In recent years, there has been growing interest in the exposure and health implications of living near major roadways as well as in related questions of whether some locations have systematically higher concentrations than others for health relevant pollutants. As a result, rapid growth of literature describing analysis of the spatial and temporal variations in observed pollutant concentrations [45] (and references therein). Characterization of the spatial and temporal variation in PM composition is crucial in order to enable a thorough understanding of the formation, transport and accumulation of PM in the atmosphere. Such knowledge is important for air quality monitoring and management [46]. Considering the aforementioned gaps in knowledge, this work aimed to determine the contribution of primary and secondary sources to the ambient PM_{10} present at different sites in the city of Augsburg. Therefore, PM_{10} samples were collected during a one-month sampling campaign from February 13 to March 12, 2008 at eight differently characterized sampling sites in Augsburg, Southern Germany. The PM_{10} samples have been analyzed for their chemical composition of organic and inorganic tracers as well as EC and OC. Receptor model of PMF [191], was applied in order to identify the main sources and quantitatively determine the contributions of the sources of ambient particles at the eight sites. Nine factors were separated comprising: solid fuel combustion, traffic-related emissions, secondary inorganics, and mixed sources. The measured PM_{10} concentrations were well explained by the modeled PM_{10} in the PMF with an R squared value of 0.96 and slope of the linear regression curve of 0.92 (Fig.19). In other words, the differences between modeled and measured PM_{10} mass were as low as possible and the PMF model has produced the lowest possible artefact.

Spatiotemporal variation of the source contributions was evaluated using the Pearson correlation coefficient (*r*) and coefficient of divergence (COD). Tables 3 and 4 show the medians of correlation coefficient and COD values for each source contribution between the eight sites. All factors (except hopanes and mixed sources) showed moderate to high ($0.6 < r > 0.8$) correlation coefficients between the eight sites and were distributed heterogeneously. Secondary sulfate and secondary nitrate factors were distributed relatively less heterogeneously compared to other factors with lower medians of COD value (0.47 and 0.56, respectively) and higher correlation values ($r = 0.97$ and 0.85, respectively).

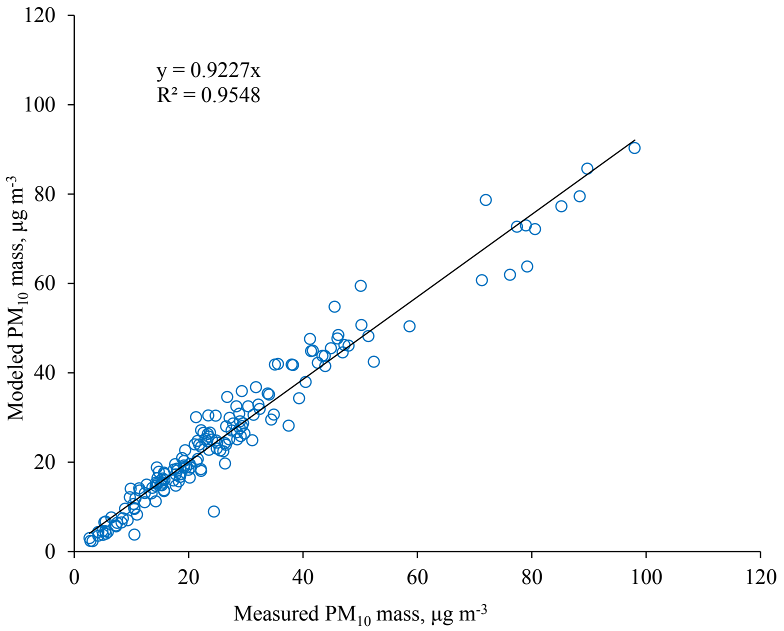


Figure 19. Linear regression of PM_{10} mass between measured and PMF modeled results at six sampling sites in February 13 -March 12, 2008. Note that PM_{10} mass concentrations were not measured at two of the sites. The modeled PM_{10} is calculated as a sum of 9 factors

The maximum daily average contribution for coal & wood combustion factor was observed at the LfU suburban site (4.0 µg/m^3); wood combustion factor at the LSW residential site (5.1 µg/m^3); diesel & fuel oil consumption factor at the Bifa suburban and BP urban sites (both 2.5 µg/m^3); road dust & tram factor at the KP traffic site (16.2 µg/m^3) and the BP urban site (6.6 µg/m^3); hopanes factor at the BP urban and Bifa suburban sites (both 0.7 µg/m^3); and de-icing NaCl factor at the KP traffic site (4.8 µg/m^3). Secondary sulfate and secondary nitrate factors had approximately similar contributions (6.2 µg/m^3 and 4.3 µg/m^3, respectively) at all sites. Mixed sources factor had the highest daily average contribution to PM_{10} mass at the KP traffic site (7.0 µg/m^3).

Table 3. Median of Pearson correlation coefficients (*r*) for the nine source factor contribution between the eight sampling sites

Factor number	Factor name	KP	BP	LSW	LfU	HT	WE	Bifa	KI
1	Coal & Wood combustion	0.80	0.85	0.79	0.83	0.65	0.75	0.85	0.62
2	Wood combustion	0.61	0.66	0.73	0.69	0.61	0.59	0.71	0.66
3	Diesel & fuel oil consumption	0.75	0.77	0.51	0.77	0.58	0.76	0.64	0.68
4	Road dust & tram	0.70	0.71	0.80	0.84	0.73	0.54	0.79	0.83
5	Hopanes	0.10	0.44	0.42	0.38	0.53	-0.01	0.40	0.07
6	De-icing NaCl	0.47	0.78	0.97	0.90	0.85	0.84	0.81	0.69
7	Secondary sulfate	0.97	0.98	0.97	0.98	0.97	0.96	0.97	0.96
8	Secondary nitrate	0.88	0.90	0.83	0.86	0.79	0.90	0.87	0.78
9	Mixed sources	-0.07	-0.06	0.15	-0.06	-0.03	-0.09	-0.03	-0.01

Table 4. Median of Coefficient of Divergence (COD) for the nine source factor contributions between the eight sampling sites

Factor number	Factor name	KP	BP	LSW	LfU	HT	WE	Bifa	KI
1	Coal & Wood combustion	0.63	0.59	0.65	0.62	0.75	0.64	0.61	0.69
2	Wood combustion	0.60	0.59	0.67	0.58	0.63	0.59	0.59	0.72
3	Diesel & fuel oil consumption	0.54	0.58	0.67	0.55	0.68	0.58	0.61	0.62
4	Road dust & tram	0.76	0.62	0.68	0.65	0.67	0.74	0.66	0.73
5	Hopanes	0.58	0.51	0.65	0.49	0.52	0.56	0.53	0.63
6	De-icing NaCl	0.66	0.52	0.58	0.45	0.47	0.56	0.51	0.71
7	Secondary sulfate	0.48	0.43	0.50	0.44	0.44	0.48	0.47	0.55
8	Secondary nitrate	0.61	0.52	0.63	0.59	0.56	0.53	0.46	0.55
9	Mixed sources	0.88	0.86	0.76	0.83	0.73	0.83	0.84	0.83

This study demonstrates that the spatial distributions of source factor contributions can be highly heterogeneous within a given air shed such as city of Augsburg. A high correlation among sites does not necessarily indicate uniformity, and particulate source composition is a dominant factor in the determination of spatial variability [49]. The results show that heterogeneous spatial variation of source contributions can exist at monitoring sites if there is heterogeneity in the distribution of local sources. In addition, the capability of PMF to resolve the main sources is dependent on the differences in the activities of the various expected sources, specifically when PM variability is predominantly driven by meteorological conditions rather than by the impact of the variability of the emission sources [192]. Therefore the PMF might also artificially increase the COD values for the source factor contributions, particularly for species which are distributed between different PMF profiles rather than a particulate profile. For example, the measured inorganic ions (sulfate, nitrate and ammonium ions) showed a very low spatial variation (median of $0.18 < \mathrm{COD} < 0.2$) between the eight sampling sites, whereas the corresponding source factor contributions for secondary sulfate and secondary nitrate as separated by PMF showed higher COD values (median of 0.47 - 0.56) between the eight sampling sites in the city of Augsburg.

5.2. Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany

Low Emission Zones (LEZ) are areas in which vehicular traffic access is restricted to vehicles that emit low levels of air pollutants only. The most severe environmental problems in Munich are caused by traffic. Vehicles with internal combustion engines contribute significantly to air pollution. In order to investigate effects of implementation of LEZ in Munich, samples of $PM_{2.5}$ were collected within the LEZ before (2006/2007) and after (2009/2010) the implementation of the LEZ. The samples were analyzed for particulate organic compounds (POC) and carbon fraction (EC/OC). Figure 13 show the difference in concentrations for some groups of compounds and selected specific compounds before and after the implementation of the LEZ.

Positive effect was detected for the implementation of LEZ on reduction of some POC concentrations but not significantly because of the variation of POC sources (see Fig. 20). The mean concentrations for most of the PAH after implementation of the LEZ were slightly but not significantly ($p>0.05$) decreased. Retene which is considered as a marker for coniferous wood combustion [193] showed a significant difference ($p<0.05$) with higher mean concentration of 0.25 ng/m^3 after the implementation of LEZ compared with 0.14 ng/m^3 before implementation of LEZ. Like for retene, significant higher concentrations of levoglucosan with significant difference ($p<0.05$) were noticed in the sampling period after the implementation of LEZ. In addition, O-PAH (which is considered beside retene and levoglocosan) as a marker for wood combustion [193-195], was observable also with higher concentrations ($p<0.05$) in 2009/10. This may be due to the colder winter in 2009/10 compared with 2006/07 and the trend of an increasing use of wood combustion for domestic heating in Germany [196]. Depending on the meteorological data provided by Bavarian State Office for Environment (Bayerischen Landesamt für Umwelt - BLfU), the temperature in winter 2009/10 ranged from -10 to 14 ^{o}C while ranged from -7 to 22 ^{o}C in winter 2006/07. Although the use of wood for domestic heating is very familiar to the general public especially in the countryside [197] nevertheless, urban areas are also impacted from local wood combustion [198].

A lower concentration of EC with significant difference ($p<0.05$) was detected after the implementation of LEZ in 2009/10. EC is regarded as an indicator for traffic emissions [84, 95], showing to some extent a positive effect of LEZ implementation. The presence of hopanes in aerosols confirmed an input from fossil fuel utilization (i.e. mainly vehicular traffic) [111]. No significant differences ($p>0.05$) in the concentrations of any of hopanes was detected when comparing mean concentrations from before and after the implementation of LEZ, but like for the PAH slightly lower concentrations were found in 2009/10. Also no significant differences ($p>0.05$) were noticed in the concentrations of the other measured POC or OC.

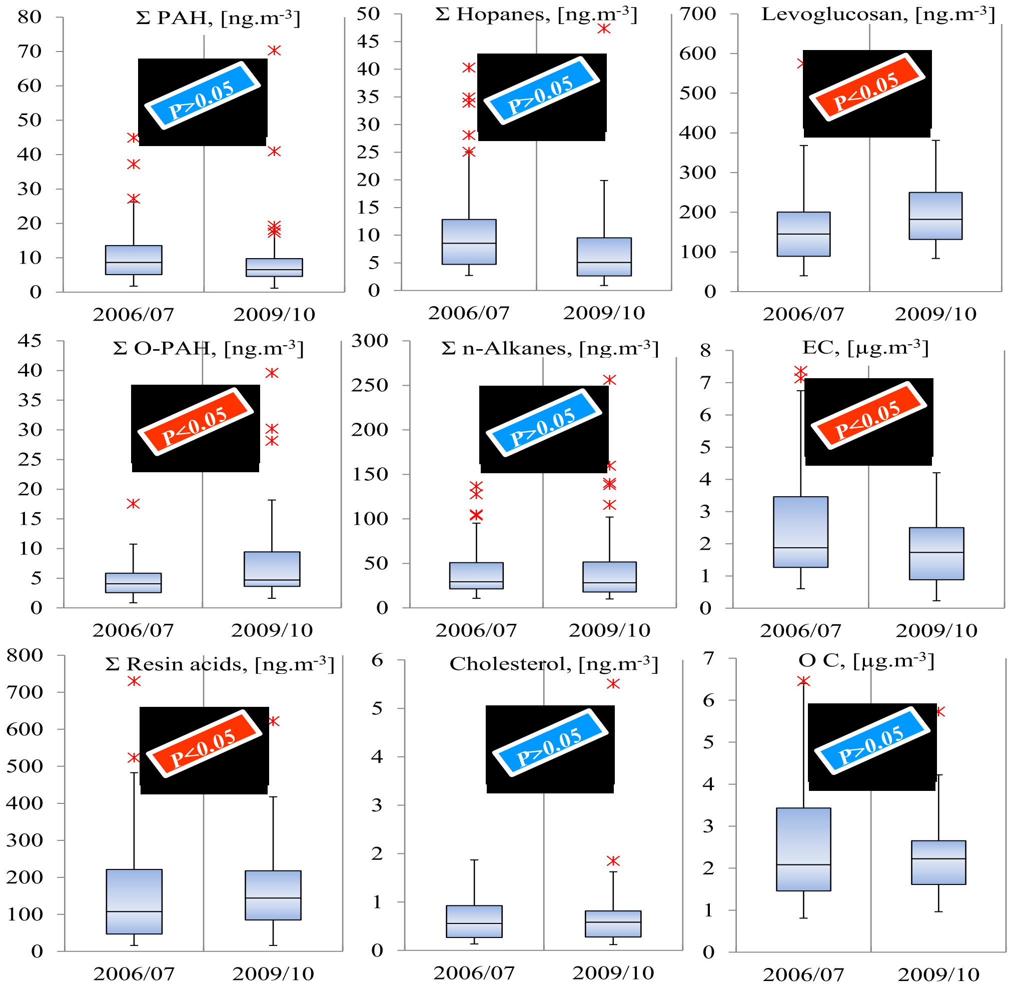


Figure 20. Boxplots of some selected POC, as groups and compounds beside the EC and OC

Concerning source apportionment, PMF model has been applied to chemical composition data in order to identify the main sources of POC. A total of 67 organic species were used for the PMF analysis beside the EC and OC. The selected species represents: PAH, O-PAH, n-alkanes, iso- & anteiso-alkanes, hopanes, resin acids, fatty acids, anhydrous sugars and phenolic compounds. The organic species with more than 33% of values under the limit of quantification (LOQ) have been excluded from the PMF input. The error fractions were increased up to 20% for each of the organic species with 10-33% of values under the LOQ. Data lower than the LOQ were replaced by half of the LOQ and their uncertainties were set to five-sixths of the LOQ [199] with no missing data. The uncertainties of the other values were calculated according to Norris [200]. PMF analyses were run with three to six factors in order to find the most reliable and best interpretable results.

The 5-factors solution was with the most reasonable interpretation of the source profiles, which were related to primary PM emissions. Traffic, first solid fuel (wood) combustion, second solid fuel (brown coal) combustion, cooking and mixed sources were the main factors separated by PMF.The results obtained by PMF analysis were expected due to the location of the sampling site which is a traffic influenced station with approximately 41 000 passing vehicles per day and the local area is mainly composed of habitation, trade and commerce [201] . Different contributions have been noticed for all five factors between the two sampling periods. The contribution of traffic and mixed sources factors decreased about 60% and 40% respectively after the implementation of the LEZ. The average concentration of EC in the traffic factor decreased from 1.1 µg/m^3 to 0.5 µg/m^3 giving a positive effect for the reduction of vehicular emissions because exposures to traffic-related EC is related to decrements in lung function [202]. Also it is worth to mentioning the legally supported car scrappage scheme (the so called “Abwrackprämie” in German) which may be also involved in the observed reduction of EC levels. In the beginning of the year 2009, during the global financial crisis, the German federal government subsided the exchange of old cars by new ones in order to support car makers. This process leads to a more environment friendly car fleet across the country as the EC emission rates of new vehicles are much lower than those of the older ones [84]. The pre-stage of LEZ implementation in Munich city also enhanced the effect of LEZ by preventing the heavy duty vehicles permanently from going through LEZ areas. The contribution of the wood combustion factor has increased in the second sampling period about 180% due to the colder winter in 2009/10 comparing with winter in 2006/07.

5.3. Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach

Schools are urban microenvironments that can account for a large portion of children’s exposure to airborne particles, which typically comprise of a large organic component. Numerous detrimental health effects have been associated with exposure to airborne particles, with children particularly susceptible. This work aimed to determine the primary sources of airborne particles that children are exposed to at school and their relative contributions by analyzing selected organic molecular markers at 11 urban schools in Brisbane, Australia. The sampling campaign for the current work was conducted from November 2011 till August 2012. Schools that were chosen were not near any large source of air pollution, other than road traffic and were also not close to any large infrastructure projects.

Application of positive matrix factorization identified four sources; vehicle emissions, biomass burning, meat cooking and plant wax emissions. Overall, the results from this study point to both local (traffic and cooking) and regional (biomass burning) primary sources influencing the levels of ambient particles that children are exposed at school, which has implications when considering potential controls to mitigate exposure at schools.

Vehicle emissions accounted for 45% of the overall OC and were characterized by C_{20-25} alkanes and the observed hopanes, with schools with the highest traffic counts generally recording the higher contributions. Biomass burning recorded high contribution to the OC (29%) and a seasonal trend was also observed that peaked in winter due to prescribed burning in bush land around Brisbane. For the same reasons, plant wax alkanes also demonstrated a similar seasonal trend, though this source only accounted for a small fraction (7%) of the OC. Cooking emissions accounted for 16% of the OC, with a school nearby a restaurant precinct recording high contributions. The contributions of source factors at the 11 schools are shown in Fig.21.

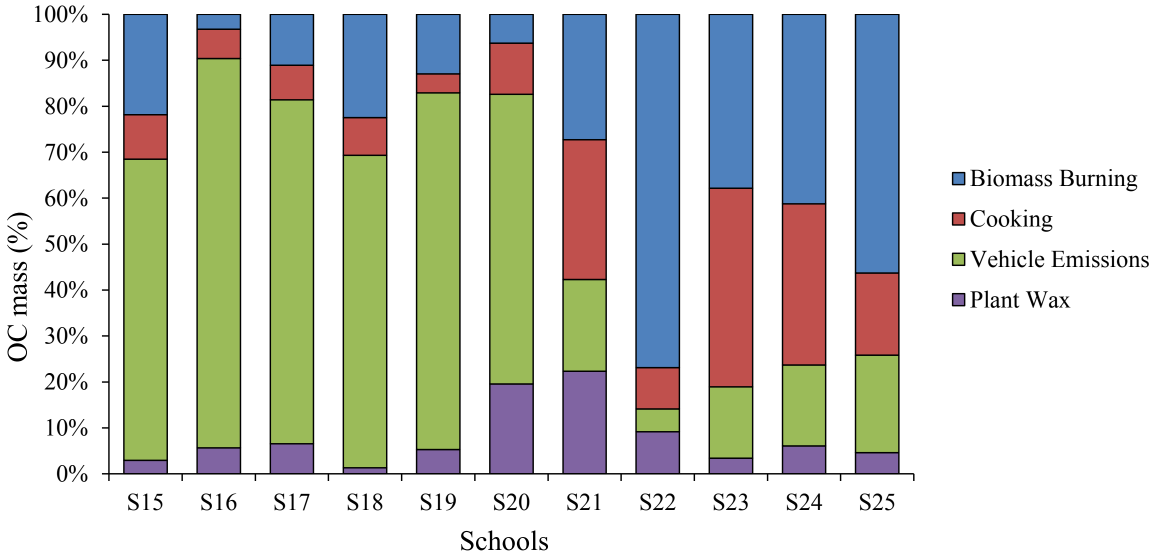


Figure 21. Percentage of PMF source factors contributions to OC mass at 11 schools under investigation

Therefore, based upon the targeted organic molecular markers, vehicle emissions were the major source of at the schools studied, confirming the hypothesis. The second largest contribution was from a more regional source, in this case biomass burning as a result of controlled burning of bush land surrounding Brisbane to reduce the risk of summer bushfires.

Controlled burning of bushland is common practice near urban areas in Australia as well as in other countries that are affected by wild bush or forest fires such as the U.S.A and Mediterranean countries. Thus the significant influence of biomass burning from both controlled and wild fires that was observed in the results from this study is potentially applicable to other urban areas in Australia and other countries. Another notable aspect of the results was the large contribution from meat cooking emissions, possibly due to activities at the schools. This result warrants further investigations to determine the full impact of meat cooking emissions at schools. Finally, although vehicle emissions were identified as a major source in this study, it is not necessarily the only major source of pollution in urban areas, as only a subset of organic compounds were analyzed in this work.

Overall, the results from this study point to the influence of both local (traffic) and regional (biomass burning) sources of primary organic aerosols on the levels of ambient particles that children are exposed at schools. This has implications for potential control measures for mitigating exposure at schools.

6. SUMMARY

Organic compounds of biogenic and anthropogenic origin often represent a large fraction, up to 40%, of total airborne PM mass and influence the behavior and impact of PM on human health. In the presented in-situ derivatization and thermal desorption of organic compounds, separation by gas chromatography and detection by time of flight mass spectrometry (IDTD GC-ToF-MS) [190] has been applied to the analysis of organic molecular marker in the PM samples which are discussed in the three publications. The advanced receptor model of Positive Matrix Factorization (PMF) [191, 200] has been applied to all organic compounds data obtained from the analysis of PM samples over the three publications to identify the possible sources of ambient PM depending on organic molecular markers and inorganic tracers. The associated contributions of organic markers have been estimated either to organic carbon (OC) fraction or to the PM mass according to PMF analysis.

There is growing interest in the exposure and health implications of living near major roadways as well as in related questions of whether some locations have systematically higher concentrations than others for health relevant pollutants. Therefore, the organic and inorganic tracers have been analyzed in PM_{10} samples, collected over a one-month sampling campaign at eight sampling sites in Augsburg, Germany. The contribution of organic and inorganic tracers to PM_{10} samples was estimated to evaluate the spatial and temporal variation of emission sources at the sampling sites. The results showed that PMF was able to identify nine source factors depending on the organic and inorganic tracers. The results also indicate that there was a heterogeneous spatial variation of source contributions at monitoring sites due to the heterogeneity of local sources.

In Munich, the most severe environmental problems are caused by traffic. Vehicles with internal combustion engines contribute significantly to air pollution. In order to investigate effects of implementation of LEZ in Munich, the analysis of the organic molecular markers in $PM_{2.5}$ samples, collected within the low emission zone (LEZ) of Munich, has been performed. The results showed that the concentration for most of the organic compounds has been decreased after the implementation of the LEZ. The Applying PMF model in this case was able to identify five source factors depending on the concentration of organic compounds. It was noticed that the contribution of traffic source factor decreased about 60% after the implementation of the LEZ.

Children are particularly susceptible to air pollution and schools are examples of urban microenvironments that can account for a large portion of children's exposure to airborne particles. Thus, the analysis of organic molecular markers in $PM_{2.5}$ samples collected at 11 different schools in Brisbane, Australia, has been employed to identify primary airborne particles that children are exposed to at school. The results showed that the application of PMF identified four sources; vehicle emissions, biomass burning, meat cooking and plant wax using organic molecular markers data. The major source was found to be traffic emissions (local source). Biomass combustion (regional source) was detected as one of the main sources in this study due to the controlled burning of bush land surrounding Brisbane to reduce the risk of summer bushfires. This study was a part of a greater study investigating exposure of children to ambient PM and related health outcomes in Brisbane, Australia.

A better understanding of the contribution of emission sources, such as regional or long range transport and local pollution sources, to the generation of elevated PM levels in different areas is of great importance. Such knowledge is important for air quality monitoring and management and as a result it is important for human health.

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APPENDIX

LIST OF ABBREVIATIONS

B[a]P	benzo[a]pyrene
BC	black carbon ”soot”
Bifa	bifa environmental institute
BLfU	bayerischen landesamt für umwelt
BP	bourgesplatz sampling site
BrC	brown carbon
C_{max}	most abundant carbon number
CMB	chemical mass balance
COD	coefficient of divergence
COPREM	constrained physical receptor model
CPI	carbon preference index
DHA	dehydroabietic acid
DHA-ME	dehydroabietic acid methyl ester
DMS	dimethy sulfoxide
DRI	desert research institute
EC	elemental carbon
EU	european union
FID	flame ionization detectors
Fig	figure
GC	gas chromatography
H_2O_2	hydrogen peroxide
HMWCs	higher molecular weight compounds
HNO_3	nitric acid
HT	hotel tower sampling site
IC	ion chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
IDTD GC-ToF-MS	in-situ derivatization -thermal desorption-gas chromatography time of flight mass spectrometry
IM	inorganic matter
IMPROVE	interagency monitoring of protected visual environments
IR	infrared spectroscopy
KI	kissing sampling site
KP	königsplatz sampling site
LEZ	low emission zone
LfU	landesamt für umwelt “environment agency”
LOD	limit of detection
LOQ	limit of quantification
LSW	lorenz-stötter-weg sampling site
MA	monosaccharide anhydrides
ME	multilinear engine
MHP	methylhydroperoxided
MSTFA	*N*-methyl-*N*-trimethylsilyltrifluoroacetamide
N_2	nitrogen gas
NH_3	ammonia gas
NH_4^+	ammonium ion

NO	nitrogen monoxide
NO_2	nitrogen dioxide
NO_3	nitrate-radical
NO_3^-	nitrate ion
NO_x	nitrogen oxides
O_3	ozone
OA	organic aerosol
OC	organic carbon
OH	hydroxyl group
OM	organic matter
OP	organic pyrolysis
O-PAH	oxidized polycyclic aromatic hydrocarbons
P	student *t-test* value
PAA	peroxyacetic acid
PAH	polycyclic aromatic hydrocarbons
PCA	principal component analysis
PM	particulate matter
PM_{10}	particulate matter with an aerodynamic diameter of less than 10µm
$PM_{2.5}$	particulate matter with an aerodynamic diameter of less than 2.5µm
PMF	positive matrix factorization
POA	primary organic aerosol
POC	particulate organic compounds
PyOC	pyrolyzed organic carbon
r	pearson correlation coefficients
ROS	reactive oxygen species
SA	source apportionment
SIA	secondary inorganic aerosol
SO_2	sulfur dioxide
SOA	secondary organic aerosol
SVOC	semi-volatile organic compounds
TCM	total carbon matter
TOR	thermal/optical reflectance
TOT	thermal/optical transmittance
UK	united kingdom
UNMIX	unmixed source apportionment
US	united states
VOC	volatile organic compounds
WE	wellenburg sampling site

LIST OF FIGURES

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LIST OF PUBLICATIONS

Peer reviewed articles

Qadir, R.M., Abbaszade, G., Schnelle-Kreis, J., Chow, J. C. and Zimmermann, R. *Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany*. Environmental Pollution **2013**. 175, 158-167.

Qadir, R.M., Schnelle-Kreis, J., Abbaszade, G., Arteaga-Salas, J. M., Diemer, J. and Zimmermann, R. *Spatial and temporal variability of source contributions to ambient PM10 during winter in Augsburg, Germany using organic and inorganic tracers.* Chemosphere **2014**,103, 263-273.

Crilley, L.R., **Qadir, R.M.**, Ayoko G., Schnelle-Kreis, J.; Abbaszade, G., Orasche, J., Zimmermann, R. and Morawska, L., *Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach.* Accepted for publication by Environmental Pollution **2014**.

Qadir, R.M., Schnelle-Kreis, J., Abbaszade, G. and Zimmermann, R. *Long-term monitoring, chemical composition and source apportionment study of $PM_{2.5}$ in Augsburg, Germany. (Article in preparation).*

Oral presentations at conferences

Qadir, R.M., Schnelle-Kreis, J., Abbaszade, G. and Zimmermann, R. *Long-term monitoring, chemical composition and source apportionment study of $PM_{2.5}$ in Augsburg, Germany.* European Aerosol Conference, **2013,** Pargue, Czech Republic.

PUBLICATIONS FOR THE CUMULATIVE DISSERTATION

PUBLICATION 1

Spatial and temporal variability of source contributions to ambient PM_{10} during winter in Augsburg, Germany using organic and inorganic tracers

by

Raeed Megeed Qadir, Jürgen Schnelle-Kreis, Gülcin Abbaszade, Jose Manuel Arteaga-Salas, Jürgen Diemer and Ralf Zimmermann

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Raeed Megeed Qadir processed all data sets, performed the positive matrix factorization (PMF) analysis and wrote the paper. The laboratory analysis of organic compounds was performed by CMA group. The analyses of elements, inorganic ions, elemental and organic carbon were performed by Bavarian Environment Agency. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

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Spatial and temporal variability of source contributions to ambient PM_{10} during winter in Augsburg, Germany using organic and inorganic tracers

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HIGHLIGHTS

- PM_{10} samples were collected in parallel during winter at eight sampling sites in Augsburg, Southern Germany.
- Particulate organic compounds (POC), total elements, inorganic ions, EC and OC were analyzed.
- PMF analysis identified nine source factors for PM_{10}.
- Pearson correlation coefficient (*r*) and coefficient of divergence (COD) indicated spatiotemporal variation.
- High spatial heterogeneity with relatively high correlations between source contributions was observed at the eight sites.

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ABSTRACT

Daily PM_{10} samples were collected during a one-month sampling campaign from February 13 to March 12, 2008 at eight different sampling sites in Augsburg, Southern Germany. Source apportionment was performed to identify the main sources and related contributions by analysis of organic and inorganic tracers. Nine factors were separated comprising: solid fuel combustion, traffic-related emissions, secondary inorganics, and mixed sources. Spatiotemporal variation of the source contributions was evaluated using the Pearson correlation coefficient (*r*) and coefficient of divergence (COD). All factors (except hopanes and mixed sources) showed moderate to high ($0.6 < r > 0.8$) correlation coefficients between the eight sites and were distributed heterogeneously. Secondary sulfate and secondary nitrate factors were relatively more uniformly distributed (compared to other factors) with lower medians of COD value (0.47 and 0.56, respectively) and higher correlation values ($r = 0.97$ and 0.85, respectively). The maximum daily average contribution for coal & wood combustion factor was observed at the LfU suburban site (4.0 $\mu g\ m^{-3}$); wood combustion factor at the LSW residential site (5.1 $\mu g\ m^{-3}$) ; diesel & fuel oil consumption factor at the Bifa suburban and BP urban sites (both 2.5 $\mu g\ m^{-3}$); road dust & tram factor at the KP traffic site (16.2 $\mu g\ m^{-3}$) and the BP urban site (6.6 $\mu g\ m^{-3}$); hopanes factor at the BP urban and Bifa suburban sites (both 0.7 $\mu g\ m^{-3}$); and de-icing NaCl factor at the KP traffic site (4.8 $\mu g\ m^{-3}$). Secondary sulfate and secondary nitrate factors had approximately similar contributions (6.2 $\mu g\ m^{-3}$ and 4.3 $\mu g\ m^{-3}$, respectively) at all sites. Mixed sources factor had the highest daily average contribution to PM_{10} mass at the KP traffic site (7.0 $\mu g\ m^{-3}$).

1. Introduction

Particulate matter (PM) is one of the most important air pollutants that adversely influences human health (Koelemeijer et al., 2006). Long term exposure to PM_{10} and $PM_{2.5}$ (particles with an aerodynamic diameter smaller than 10 and 2.5 μm, respectively) has been associated with effects on breathing and the respiratory system, lung tissue damage, cancer, and both cardiovascular mortality and morbidity. Epidemiological and toxicological studies have shown that PM mass comprises different fractions with varying types and degrees of adverse health effects, suggesting a role for both the chemical composition and physical properties of PM (WHO, 2013). In the last few years, there has been a rapid growth of literature describing analysis of the spatial and temporal variations in the concentrations of ambient PM has been observed (Levy and Hanna, 2011).

Potential for the misclassification of population-average ambient exposures of communities exists due to spatial variability of

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PM concentration when a limited number of ambient PM monitors are used. A better understanding of the contribution of factors, such as regional and long range transport of PM, local pollution sources or other processes, to the generation of elevated PM levels in urban areas is of great importance (Juda-Rezler et al., 2011). Characterization of the spatial and temporal variation in PM composition is crucial in order to enable a thorough understanding of the formation, transport and accumulation of PM in the atmosphere; such knowledge is important for air quality monitoring and management (Zheng et al., 2013).

Positive matrix factorization (PMF), an advanced receptor model (Paatero, 1997, 1999), has previously been successfully used for quantitative identification of the sources of organic and inorganic pollutants in aerosol samples from Augsburg, Germany (Schnelle-Kreis et al., 2007; Gu et al., 2013). More recently, a study of the spatial and temporal variation of PM in Augsburg was reported by Gu et al. (2013), in which the sources of ambient PM_{10} in samples collected during winter 2006/07 and winter 2007/08 were apportioned on the basis of their chemical composition (elements, ions, and carbon fractions). In our present study, source apportionment was carried out using organic and inorganic tracers for daily PM_{10} samples collected during a one-month sampling campaign from February 13 to March 12, 2008 at eight sampling sites in Augsburg, Germany.

2. Methodology

2.1. Sampling campaign and sites

Daily PM_{10} samples were collected over a one-month sampling campaign from February 13 to March 12, 2008 at eight sampling sites in Augsburg, Germany. An additional three-month pre- and post-sampling phase was conducted at the central sampling site of the Königsplatz (KP). Fig. 1 shows the location of the eight sampling sites used in this study.

Augsburg is a medium-sized city in Southern Germany with a population of 265 000. The Königsplatz (KP) site is located in the city center close to roads with a high traffic density (30 500 cars per day in the year 2000); therefore, KP was considered an urban traffic site. The Bourgesplatz (BP) site is located in a small park and is about 1 km north of the KP site. As a major road and a tramline are located about 70 m north of the BP site, this site was considered a traffic-influenced urban background site. The LSW (Lorenz–Stötter–Weg) site is located in a residential area where home heating is expected to have a greater influence on PM levels in the winter. The LfU site is located on the premises of the Bavarian Environment Agency (LfU) approximately 4 km south of the city center and was considered an urban background site. The Hotel Tower (HT) site was conducted on the rooftop of the tallest building in Augsburg, about 100 m above the ground. The HT site lies within the boundary layer which normally represents the urban background. In situations of very low mixing layer heights – which occurred during three periods of our sampling campaign – the HT site could also represent the regional background. The Wellenburg (WE) site is located in Southwestern Augsburg next to the natural park, and was considered a suburban background site. The Bifa site is located close to the Bifa Environmental Institute in northeast of Augsburg; therefore, this site was considered a suburban background site. The Kissing, Gut Lindenau (KI) site, another suburban background site, is located about 1 km north of the town of Kissing and about 9 km southeast of Augsburg. Table 1 summarizes the characteristics of the sampling sites.

2.2. Sampling and chemical analysis

PM_{10} was collected on quartz fiber filters (Whatman International Ltd., Maidstone, England) using a high volume sampler (Digitel DHA 80, Volketswil, Switzerland) at a flow rate of 500 L min^{-1}. Each sampling period was 24 hours from 00:00 to 24:00. One filter was used as field blank every week. Prior to sampling, the quartz fiber filters were baked for at least 12 h in a circulating air oven (Nabertherm, Lilienthal, Germany) at 500 °C to remove all organic matter. Samples were stored in glass containers at −18 °C until analysis. PM_{10} mass data was available for all sites except the LSW and HT sites. Samples were analyzed for particulate organic compounds (POC), elemental carbon and organic carbon fractions (EC/OC), water-soluble inorganic ions, and total elements.

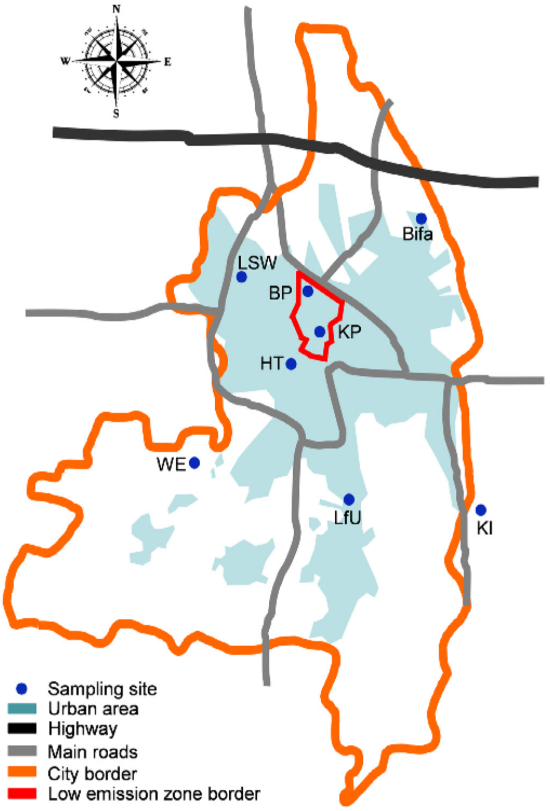


Fig. 1. Location of the eight sampling sites in Augsburg.

In situ derivatization thermal desorption gas chromatography time-of-flight mass spectrometry (IDTD-GC-ToF-MS) (Orasche et al., 2011) was employed for quantification of POC in the samples. Metal composition was determined by inductively coupled plasma mass spectrometry (ICP-MS) using rhodium and lutetium as internal standards. The concentration of water-soluble ions was analyzed by ion chromatography (IC). EC and OC fractions were determined according to VDI 2465. In Germany, VDI 2465 Part 1 & 2, a method involving extraction of OC by toluene and 2-propanol, thermodesorption in a nitrogen flow and subsequent combustion has been established a standardized technique in addition to the thermal method (Schmid et al., 2001). A list of the target analytes is provided in Table 2 in the Supplementary Material (SM1).

2.3. Positive matrix factorization

Positive matrix factorization (PMF) is an advanced factor analysis technique based on a weighted least-squares fit and error estimates of the measured data. PMF was developed by Paatero (1997, 1999) and considers data uncertainty in its assessment of source

Table 1
Sampling sites specifications.

Sampling site	Abbreviation	Sampling site characteristic	Sampling	
			Start dd/mm/yyyy	End dd/mm/yyyy
Königsplatz	KP	City center, traffic	14.11.2007	31.03.2008
Bourgesplatz	BP	Urban background	13.02.2008	12.03.2008
Lorenz-Stötter-Weg	LSW	Residential	13.02.2008	12.03.2008
Bavarian environment agency	LfU	Urban background	13.02.2008	12.03.2008
Hotel tower	HT	Urban, 100 meters height	13.02.2008	12.03.2008
Wellenburg	WE	Sub-urban background	14.02.2008	12.03.2008
Bifa environment institute	Bifa	Sub-urban background	13.02.2008	12.03.2008
Kissing, Gut lindenau	KI	Sub-urban background	14.02.2008	12.03.2008

profiles and source contributions. The model used in this study was EPA-PMF 3.0, which was developed by the US EPA and is based on the ME-2 algorithm (US-EPA, 2008).

Source apportionment for our study was performed using data collected from the eight sampling sites during the one-month sampling campaign from February 13 to March 12, 2008. For data below the limit of quantification (LOQ), the values were replaced by half of the LOQ and the uncertainty was set to 5/6 of the LOQ (Polissar et al., 1998). For other data, the uncertainties (u) were set according to the following equation:

$$u = [(\text{error fraction} \times \text{concentration})^2 + (\text{LOQ})^2]^{0.5} \qquad (1)$$

where the error fraction is the percentage of uncertainty, and LOQ is the limit of quantification. Error fractions were estimated from sampling and analytical errors.

Data from all eight sampling sites were combined and analyzed together in the PMF matrix. In total, 230 daily samples were used for PMF analysis. Due to malfunction of the sampler, the data of 4 sampling days at the LSW site and 6 other sampling days at the KI site were excluded from the PMF runs. A total of 79 POC for each sample were used in the initial PMF analyses in addition to the elements, ions, EC/OC and the PM_{10} mass. PM_{10} mass data was available for all sites except the LSW and HT sites. Therefore, the PM_{10} mass for the LSW and HT sites were considered as missing data and were replaced by the mean PM_{10} mass of the other six sites and the associated uncertainty values were of four times of the mean. In general, POC with less than 80% in the particle phase were excluded from the PMF analysis. Other POC such as: nonadecane, 17β(H)-22,29,30-trisnorhopane (27b), isopemaric acid, abietic acid, mannosan, and phenolic compounds were also characterized as "bad" species because of their low signal-to-noise ratio ($S/N < 0.2$). Characterization of Tl as "bad" specie was necessary as a large percentage of the values were below the limit of quantification (data coverage < 33%). The final PMF data matrix was conducted for 230 daily samples with 84 variables (including 60 POC). PMF analysis with a nine-factor solution was chosen as the most reasonable interpretation of the factors related to different emissions.

A sensitivity analysis of the PMF model was performed to examine the impact of the number of factors selected for the PMF computation with the most reasonable interpretation. Varied numbers of PMF factors from 6 to 10 were examined to assess the consistency of the PMF solution with the current understanding of the source profiles. Further details of the PMF sensitivity tests and species categories (Table 3a and b) are provided in the Supplementary Material (SM2).

2.4. Statistical analysis

Spatiotemporal variability was conducted by evaluating the Pearson correlation coefficient (r) in conjunction with the coefficient of divergence (COD) for each factor contribution between eight sites. The Pearson correlation coefficient reflects the linearity of the relationship between variables. The COD provides information on the degree of uniformity of particulate air pollutants between the sampling sites. COD is a measure of the relative heterogeneity of the concentrations between sites, ranging from 0 to 1. A low COD value (<0.2) indicates a high level of homogeneity between sites, while COD values larger than 0.2 indicate heterogeneous sites (Wilson et al., 2005). COD was determined using:

$$\mathrm{COD}_{jk} = \sqrt{\frac{1}{P}\sum_{i=1}^{P}[(x_{ij} - x_{ik})/(x_{ij} + x_{ik})]^2} \qquad (2)$$

where x_{ij} and x_{ik} represent the observations for sampling day i at sampling sites j and k, and where p is the number of observations.

3. Results and discussion

3.1. PMF source profiles

The nine-factor solution was selected for this study. The factor profiles are shown in Fig. 2. Each one of these factors was characterized by a pattern of species which could be associated with a specific source or with groups of sources. The separated factors represent: two solid fuel combustion-related factors (coal & wood combustion; wood combustion), four traffic-related factors (diesel & fuel oil consumption; road dust & tram; hopanes; de-icing NaCl), two secondary inorganic factors (secondary sulfate; secondary nitrate), and a mixed sources factor (traffic, cooking and tobacco smoke).

3.1.1. Solid fuel combustion-related factors

Factor one (coal & wood combustion) was dominated mainly by hopanes, polycyclic aromatic hydrocarbons (PAH), oxidized polycyclic aromatic hydrocarbons (O-PAH), levoglucosan, and potassium, while factor two (wood combustion) was characterized by levoglucosan, potassium, PAH, and a high percentage of O-PAH. Levoglucosan is a pyrolysis product of cellulose and hemicelluloses and has been proposed as a marker of biomass combustion (Simoneit, 1999). Although it was reported that levoglucosan was not detectable in coal smoke samples (Oros and Simoneit, 2000), the presence of unusually high levels of levoglucosan in brown coal pyrolysates suggests that a portion of this compound in some air sheds may also originate from lignite combustion (Fabbri et al., 2008). Potassium is often used as a marker for wood smoke (Schauer et al., 1996), and PAH and O-PAH are well associated with biomass combustion (Schnelle-Kreis et al., 2007).

Hopanes are constituents of all mineral oil- or coal-based fuels and lubricants (Kaplan et al., 2001), and have been identified in emissions from coal burning (Oros and Simoneit, 2000), heating oil burning, and vehicles (Rogge et al., 1997). The homohopane index (31abs/31abs + 31abR) (Schnelle-Kreis et al., 2007) for coal combustion aerosols increases with increasing coal maturity

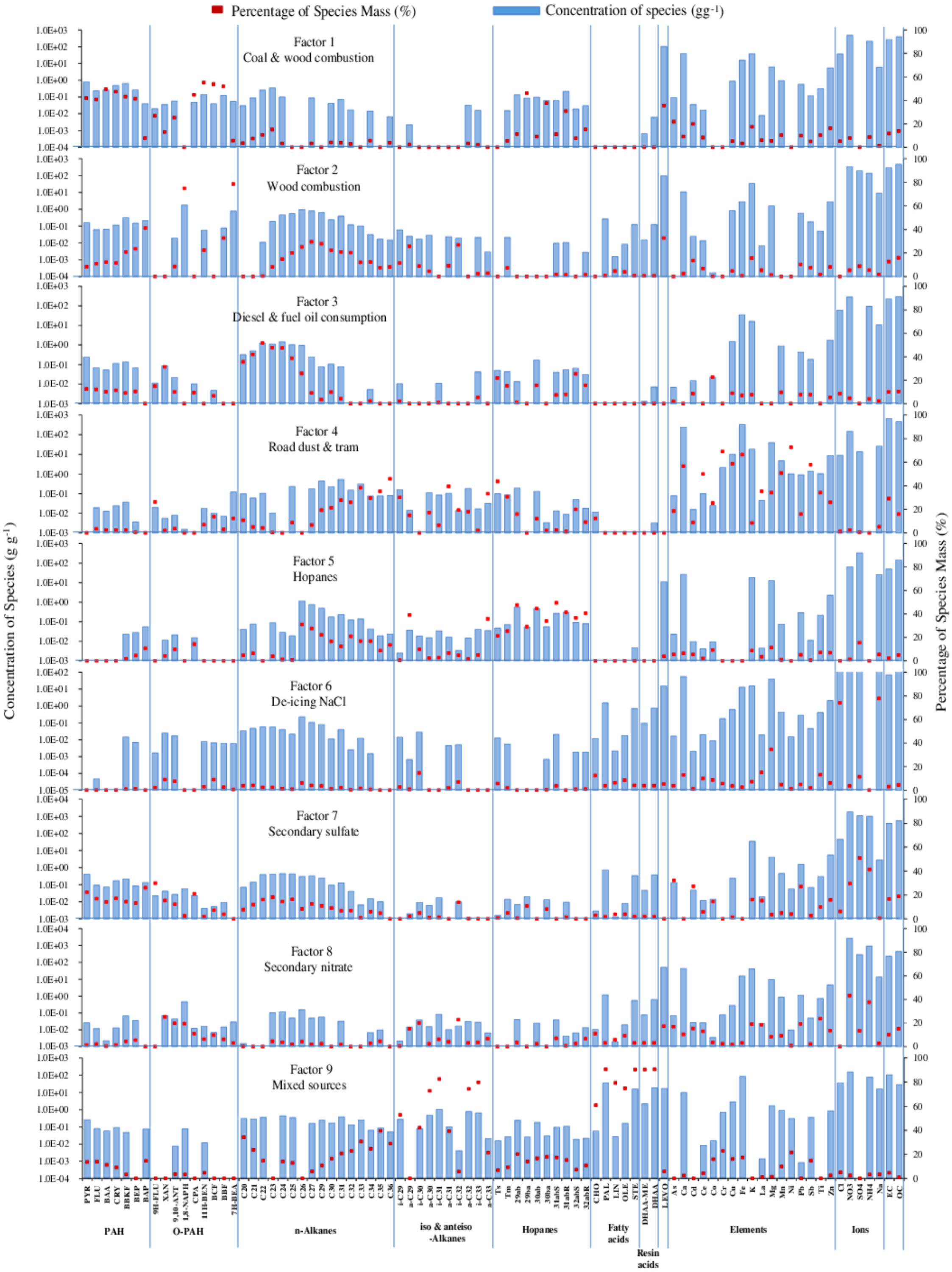


Fig. 2. PMF factor profiles obtained from a one-month sampling campaign from February 13 to March 12, 2008 at eight sampling sites in Augsburg. Concentration (g g^{-1}) is the mass of species contained in every 1 g of particles in a factor profile. Percentage of species mass (%) is the concentration of a species contained in one factor divided by total factor concentration.

(Bi et al., 2008) but is higher in mineral oil-based sources. The homohopane index found in emissions from coal combustion ranges from approximately 0.1 for lignite coal to approximately 0.4 for bituminous coal, and ranges from 0.54 to 0.67 for vehicular emissions and fuel oil consumption (Schnelle-Kreis et al., 2007).

The homohopane index for factor one was 0.2, indicating a contribution of coal combustion. The use of lignite briquettes (brown coal) is common practice for keeping a fire going overnight in wood burning stoves during the winter in Germany; therefore, factor one was regarded as coal & wood combustion factor. Factor two was mainly dominated by levoglucosan, potassium, O-PAH, and some PAH; therefore, factor two was considered as wood combustion factor. It is worth mentioning that about 25% (38 t/a) of the local PM_{10} in Augsburg is emitted from wood combustion (Brandt et al., 2011).

3.1.2. Traffic emission-related factors

The four factors related to traffic were: factor three (diesel & fuel oil consumption), factor four (road dust & tram), factor five (hopanes), and factor six (de-icing NaCl). These separate factors were characterized according to their hopane patterns and n-alkane profiles, in addition to their characteristic elements.

The homohopane index values for the diesel & fuel oil consumption, road dust & tram, and hopanes factors were 0.42, 0.6, and 0.48, respectively, indicating the mineral oil-based sources of vehicular emissions and related fuel oil consumption. The n-alkanes are an important class of organic compounds in ambient aerosols, and their homologue distribution may indicate different pollution sources (He et al., 2006). An n-alkanes profile (C_{max}) between C_{23} and C_{25} serves as a marker for diesel exhaust, whereas a $C_{max} \geqslant C_{27}$ indicates inputs arising from higher plant waxes (Shweta et al., 2013), while n-alkanes with a chain length around C_{20} mostly originate from unburned fuel (Brandenberger et al., 2005). Factor three (diesel & fuel oil consumption) was characterized by more than 50% of C_{23}–C_{25} (from diesel exhaust) and approximately 40% of C_{20} (most probably from fuel oil consumption). Diesel-powered vehicles are quite popular in Germany due to their lower fuel costs in comparison with gasoline-powered vehicles. Recently, diesel-powered vehicles accounted for 48% of newly-registered cars in the year 2012 in Germany. Therefore, factor three was regarded as diesel & fuel oil consumption factor.

Factor four was associated with high concentrations of Ca, Mg and Fe, which are mainly of crustal origin (Han et al., 2007). Traffic impact was also associated with this factor due to its high concentration of Cu, Sb and Ce, in addition to 30% of EC; EC is commonly associated with motor vehicle emissions (Shrivastava et al., 2007). Besides, high contents of trace elements such as Ni, Mn, Cr, Ti and Co were also observed in this factor. These elements and a part of the Fe content most probably derive from tram lines. Metals including Fe, Cr, Ni and Mn are components of steel, and are likely to derive from the friction between the tram wheels and rails, as well as between the pantograph and catenary. These particles, usually appearing as coarse particles, will be re-suspended in the air by passing vehicles.

The carbon preference index (CPI), defined as the ratio of the concentration of odd- to even-carbon numbered n-alkanes, has been widely used to evaluate biogenic and anthropogenic contributions to organic aerosols. Urban environments, with large contributions from anthropogenic emissions, generally exhibit CPIs ranging between 1.1 and 2.0, while rural environments with larger biogenic impacts generally exhibit CPIs above 2.0 (Brown et al., 2002). The CPI value for factor four (road dust & tram) was 2.9, indicating an impact of biogenic sources of n-alkanes (most probably plant waxes). As a result, factor four was considered road dust & tram factor, separated from traffic emissions.

In contrast, the CPI value for factor five (hopanes) was 0.9, similar to the CPI values for vehicular emissions which are close to unit (CPI ≈ 1) (Kavouras et al., 1999). In combination with its homohopane index of 0.48, this factor was regarded as particular factor of hopanes, which are most probably emitted by local traffic.

Factor six was characterized by high concentrations of Na^+ and Cl^- and could explain more than 75% of the content of both Na^+ and Cl^-. Road-safety maintenance during wintertime in areas affected by snow and ice includes the use of de-icing salts (NaCl). The re-suspension of de-icing agent used in winter is the most probable source of NaCl.

3.1.3. Secondary inorganic-related factors

Factor seven was mainly dominated by sulfate and ammonium ions. High percentages of elements such as As, Pb and Cd were also associated with this factor. These elements, in addition to SO_2, are emitted from coal-fired power plants (Nalbandian, 2012), and are the main contributors to secondary sulfates in Central Europe. In contrast, factor eight was characterized by approximately 40% of both nitrate and ammonium ions. Therefore, these two factors were considered as secondary sulfate and secondary nitrate, respectively.

3.1.4. Mixed sources-related factor

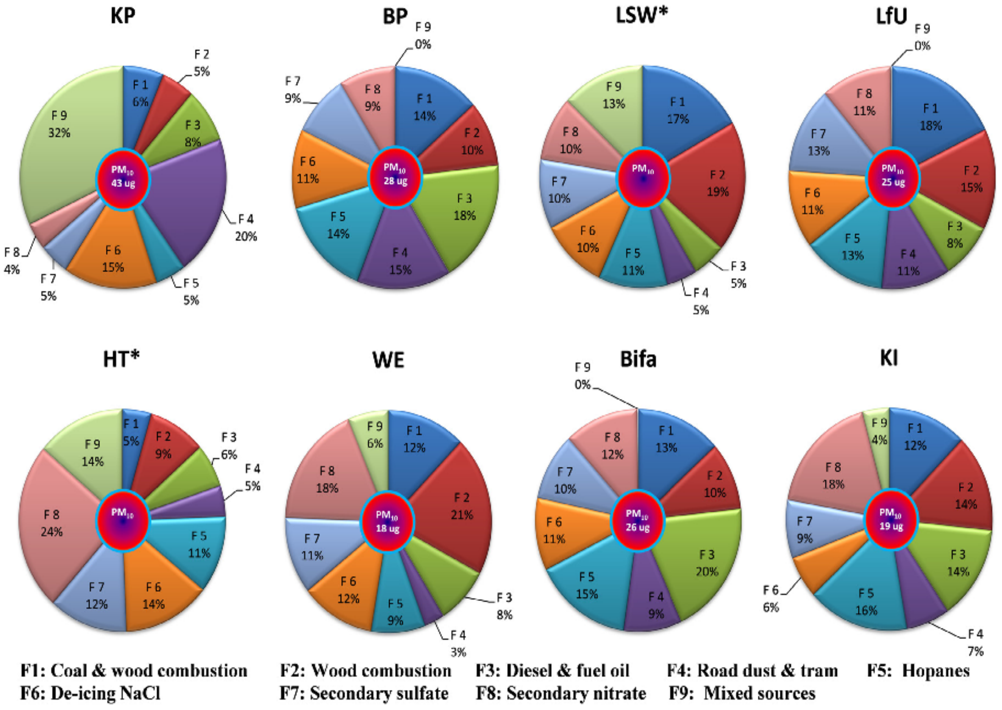
The ability of PMF to resolve the main sources depends on differences in the activities of the various expected sources, especially when the PM variability is predominantly driven by meteorological conditions rather than by the variability of the emission sources. Therefore, the identification of mixed sources factors instead of those of unmixed sources cannot be excluded (Gianini et al., 2013).

Factor nine (mixed sources) was dominated by cholesterol, fatty acids, a characteristic pattern of iso- and anteiso-alkanes, n-alkanes, hopanes, and dehydroabietic acid. About 80% of cholesterol and up to 90% of fatty acids which are markers of cooking emissions (Shrivastava et al., 2007), were associated with this factor. Tobacco smoke was also associated with factor nine due to the high load of iso- and anteiso-alkanes pattern characteristic of the tobacco leaf surface, which are considered as markers for tobacco smoke (Rogge et al., 1994). All fatty acids between C_{10} and C_{26} with palmitic acid as the major saturated component and linolenic acid as the major unsaturated component, have been reported to be present in tobacco smoke (Mold et al., 1966). More than 90% of palmitic acid was found in factor nine. Additionally, n-alkanes with a CPI of 2.1 – within the range of the CPI value for tobacco smoke in urban areas (Finlayson-Pitts et al., 2000) – were also attributed to this factor. Hopane patterns from mineral oil-derived emissions (homohopane index of 0.47) were also attributed to factor nine. The dehydroabietic acid signal often exhibits a strong correlation with the measured ambient PM concentrations due to its presence in both plant residues and car tires (Sheya, 2002). About 90% of dehydroabietic acid, most probably deriving from car tires, was associated with this factor. Thus, this source factor could be interpreted as mixed cooking, tobacco smoke, and traffic emissions factor.

3.2. Source factor contributions to PM_{10}

The contribution percentage of each source factor and the average of measured PM_{10} mass for the eight sampling sites are shown in Fig. 3 (PM_{10} mass for the LSW and HT sites were not determined). The measured PM_{10} concentrations are well explained by the modeled PM_{10} in the PMF with an R squared value of 0.96 and slope of the linear regression curve of 0.92. Detailed information is provided in the Supplementary Material (SM3).

Both the coal & wood combustion and the wood combustion factors exhibited very similar average levels of contribution at all



* PM_{10} mass were not measured for LSW and HT sites

Fig. 3. Percentage of factor source contributions and average of measured PM_{10} mass at the eight sampling sites in Augsburg.

sites (average of 2.7 μg m^{-3} and 2.8 μg m^{-3}, respectively). The coal & wood combustion factor contributed a maximum daily average of 4.0 μg m^{-3} to the PM_{10} mass at the LfU site (urban background), while the wood combustion factor exhibited the highest daily average contribution of 5.1 μg m^{-3} to the modeled PM_{10} mass at the LSW (residential background site). This agrees with the fact that using wood combustion for local heating purposes has a substantial impact at the LSW site.

The average contribution level of the diesel & fuel oil consumption factor was 1.3 μg m^{-3}; however, the maximum daily average contribution of this factor was 2.5 μg m^{-3} which was observed at both the Bifa and BP sites. This result appears to be in contrast to the fact that Bifa is a suburban site; however, it can be explained by the fact that the Bifa site is near to a major highway, as well as to the waste incineration plant for the city of Augsburg which is located less than 1 km north of the site. All of the heavy duty trucks delivering waste to the incineration plant pass close by the Bifa site. Furthermore, as confirmed by meteorological data, the wind was predominantly blowing from the north during the sampling period, which also may have also enhanced the impact of the major highway traffic to this factor contribution. The high level contribution of the diesel & fuel oil consumption factor at the BP site was expected due to the location of this site near to major roads. In addition, a large factory producing ship engines (MAN Diesel & Turbo, the largest industrial plant in Augsburg) is located about 1 km northeast of the BP site. The prominent influence of diesel and fuel oil consumption at the Bifa and BP sites is most probably a result of the heavy duty trucks passing close by both the Bifa and BP sites, as stated above.

The road dust & tram factor exhibited highly variable source contributions. The lowest daily average contribution (1.6 μg m^{-3}) occurred at the WE site, while the highest levels of 6.6 μg m^{-3} and 16.2 μg m^{-3} were observed at the BP and KP sites, respectively. Both the BP and KP sites are mainly affected by traffic and traffic-related emissions such as re-suspended road dust. In addition, tram-related emissions could be detected due to the fact that the central tram station is located close to the KP site and a main tram-line is runs near the BP site.

The highest daily average contribution (0.7 μg m^{-3}) of the hopanes factor (from vehicular emissions) was observed at the BP and Bifa sites. The high contribution of the hopanes factor at these sites could be explained by the location of major roads near to the BP site and the location of a highway close to the Bifa site. Depending on the wind direction and dispersion conditions, the impact of local traffic sources had a significant influence at the BP and Bifa sites. In contrast, the lowest daily average contribution for the hopanes factor (0.28 μg m^{-3}) occurred at the WE site, which could be explained by the lower influence of traffic emissions at this suburban site.

The lowest contribution of the de-icing NaCl factor (daily average of 1.3 μg m^{-3}) occurred at the KI site and the highest (daily average of 4.8 μg m^{-3}) was observed at the KP site. Re-suspension of de-icing agent leads to relatively large particles, causing increased PM_{10} concentrations in the vicinity of traffic-related sites, explaining the increased factor contribution at the KP site.

The average contribution of the secondary sulfate and secondary nitrate factors at all sites were approximately 6.2 μg m^{-3} and 4.3 μg m^{-3}, respectively. The highest daily average contribution (8.4 μg m^{-3}) of secondary sulfate occurred at the LfU site, whereas the maximum daily average contribution of the secondary nitrate factor (6.8 μg m^{-3}) was observed at the HT site (100 meters above the ground). The HT site normally lies within the boundary layer representing the urban background. In cases of very low mixing layer heights – which occurred during three periods of our sampling campaign – the HT site could also represent the regional background. The high contribution of secondary inorganics at the LfU and HT sites could be a result of the even distribution of secondary inorganics over the entire study area as indicated by their low COD values (Section 3.3).

The maximum daily average contribution of the mixed sources factor (7.0 μg m^{-3}) was observed at the KP site and the lowest contribution of 0.4 μg m^{-3} at the KI site (suburban background). The KP site represents a city center background in Augsburg which is impacted by different emissions (mainly traffic-related emissions). The high contribution of the mixed sources factor at the KP site (17-fold higher than at the other sites) could be explained by the impact of traffic emissions as well as of cooking and vending of food such as fast food, and hotdogs in this area.

The contribution of different sources to the PM_{10} mass at the eight sampling sites (see Fig. 3) indicates that the particle sources are site-dependent. For example, the mixed sources factor – which most probably represents the city center background – contributes to about 32% of the PM_{10} mass at the KP city center traffic site. Additionally, the highest contribution of solid fuel combustion (36%) was observed at the LSW site (residential background), indicating the strong local influence of solid fuel domestic heating rather than other sources in areas with a high number of detached houses.

3.3. Spatiotemporal variation of source factors

Fig. 4 presents the spatiotemporal variation of each factor contribution at the eight sampling sites in Augsburg city from February 13 to March 12, 2008.

To investigate the variability of different source factor contributions, the Pearson correlation coefficient (r) and coefficient of divergence (COD) were calculated for each source factor contribution between eight sites (see Table 4a and b in Supplementary Material SM4). The Pearson correlation coefficient reflects the linearity of the relationship between two variables and ranges from +1 to −1. A high Pearson correlation coefficient indicates similar temporal variation patterns, but does not necessarily mean similar levels of factor contributions at different sites. The homogeneity of distribution can be evaluated using the COD. COD is a measure of the relative concentration heterogeneity between sites and ranges from 0 to 1. A low COD value (<0.2) indicates a high level of homogeneity in concentrations between sites, while a COD larger than 0.2 indicates heterogeneous sites (Wilson et al., 2005).

The average Pearson correlation coefficients (r) and COD for the nine source factor contributions between the eight sites are shown in Fig. 5a and b.

In general, the medians Pearson correlation coefficients between the eight sites were moderate to high ($0.6 < r > 0.8$) for all factors, except the hopanes and mixed sources factors which showed the lowest correlation between all sites. Furthermore, the correlations between the KP site and other sites were relatively low, especially for traffic-related source factors. The median COD for the nine factors between the eight sites ranged from 0.47 to 0.83, revealing the high spatial heterogeneity of the source factor contributions. The lowest COD value (lowest spatial variation of factor contributions) was observed for the secondary sulfate factor (COD of 0.43) between the BP site and other sites, while the highest COD value of 0.88 was observed for the mixed sources factor between the KP site and other sites.

Factor one (coal & wood combustion) exhibited a high median Pearson correlation coefficient of 0.76 between all sites. The lowest temporal correlation ($r = 0.62$) was found for factor one between the KI and other sites. This could be explained by the fact that KI is a suburban site located outside the city of Augsburg. Whereas factor two (wood combustion) showed a slightly lower correlation (median of 0.66) between all sites. The HT site showed the lowest temporal correlation ($r = 0.61$) with other sites. HT site is quite distinct from the other sites, due to the site specification of HT which is a tower site (100 meters above ground) and normally lies within the boundary layer representing the urban background. Factor one and factor two had a medians COD value of 0.68 and 0.64, between eight sites respectively, indicating that solid fuel combustion pollutants were distributed heterogeneously over the city area, with higher temporal variation trends at the urban and residential backgrounds like the LfU and LSW sites.

Diesel & fuel oil consumption (factor three) exhibited moderate to high Pearson correlation coefficients in the range of 0.5–0.8 between the eight sites. The lowest temporal correlation for this factor was observed between the LSW site ($r = 0.51$) and other sites as well as between the HT site ($r = 0.58$) and other sites. The LSW and HT sites showed lower temporal trends of this factor (see Fig. 4). In contrast, the BP site was observed with highest temporal trend in the first half of the sampling period; while in the second half of the sampling period, the highest temporal trend was occurred at the Bifa site. This factor showed also a high spatial variation; median COD value of 0.58 between all sites. A two-fold of higher concentration of this factor was detected at both the BP and the Bifa sites compared to the other sites (see Section 3.2 above).

Road dust & tram (factor four) showed a high Pearson correlation coefficient (r) between all sampling sites, with a median value of 0.8. This factor, however, was distributed heterogeneously with a median COD value of 0.69 between the eight sampling sites. A lower temporal correlation was detected between the KP and other sites as well as between the BP and other sites. Higher temporal variation trends of this factor were observed at the KP and BP sites. Both the BP and KP sites are mainly affected by traffic and traffic-related emissions such as re-suspended road dust. On the other hand, the WE and HT sites had the lowest temporal variation trend for factor four. As previously mentioned, HT is a tower site (100 meters above the ground) and WE is a suburban site with less impact of traffic-related emissions, and both of these sites are distinct from the other sites located close to the city center. The contribution of this factor at the KP was 10 times; at BP was 4 times of the lowest contribution at the WE site (16.2 & 6.6 vs. 1.6 μg m^{-3}).

Factor five (hopanes) exhibited a very weak median of correlation coefficients ($r = 0.29$) and a high spatial variation (median COD of 0.57) between all eight sites (as shown in Fig. 5a and b). One potential reason for the low correlation and the high spatial variation of this factor may be the highly variable impact of local particulate sources on the factor contribution.

In general, de-icing NaCl (factor six) showed a strong median correlation ($r = 0.8$) and a high COD value of 0.57 between all sites. This factor showed a distinct temporal trend behavior in the first half of the sampling period at the KP site, which is a traffic-related site (see Fig. 4); the median of the correlation coefficients between the KP site and the other sites was approximately 0.47. In contrast, de-icing NaCl exhibited stronger correlations between the other seven sites, with median of the correlation coefficients (r) of 0.70–0.97. The low correlation of the de-icing NaCl factor between the KP site and the other sites in the first half of the daily sampling campaign (before February 27) was due to the probable application of high level of de-icing agent at the traffic-related KP site in February 2008 and the intensive re-suspension of de-icing NaCl. Snowfall was recorded on February 15, 2008, followed by sunny days with no rain or snowfall. Therefore, re-suspension of de-icing agent at the major road in the vicinity of the KP site during the dry period after application of de-icing salt led to the elevated concentrations of the de-icing NaCl factor at this site. Slightly increased contributions of this factor were also observed at the BP site during this period.

Secondary sulfate (factor seven) and secondary nitrate (factor eight) were highly correlated between all monitoring sites (see Fig. 4), with medians of Pearson correlation coefficients (r) of 0.97 and 0.85, respectively. Both factors showed very consistent temporal variations between the eight sites. The lowest COD values

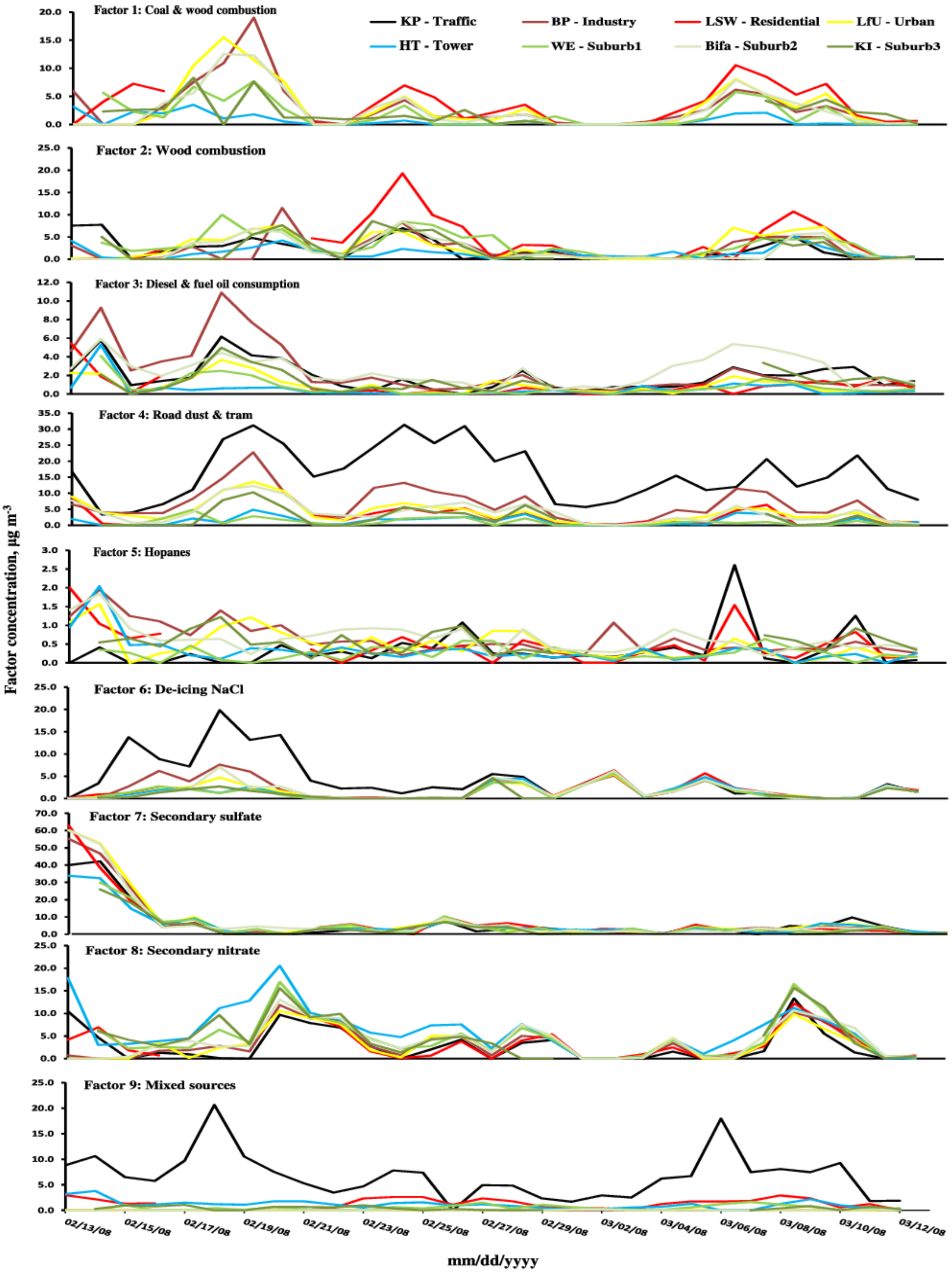


Fig. 4. Spatiotemporal variation of the nine source factor contributions at the eight sampling sites between February 13 and March 12, 2008 in Augsburg.

compared to other factors (but still high) were observed for long-range transported aerosol: secondary sulfate factor (median COD 0.47) and secondary nitrate (median COD 0.56), indicating that secondary aerosol is more uniformly distributed over the whole study area compared to other factors. It is clear from Fig. 4 that the mixed sources factor (factor nine) showed a significantly

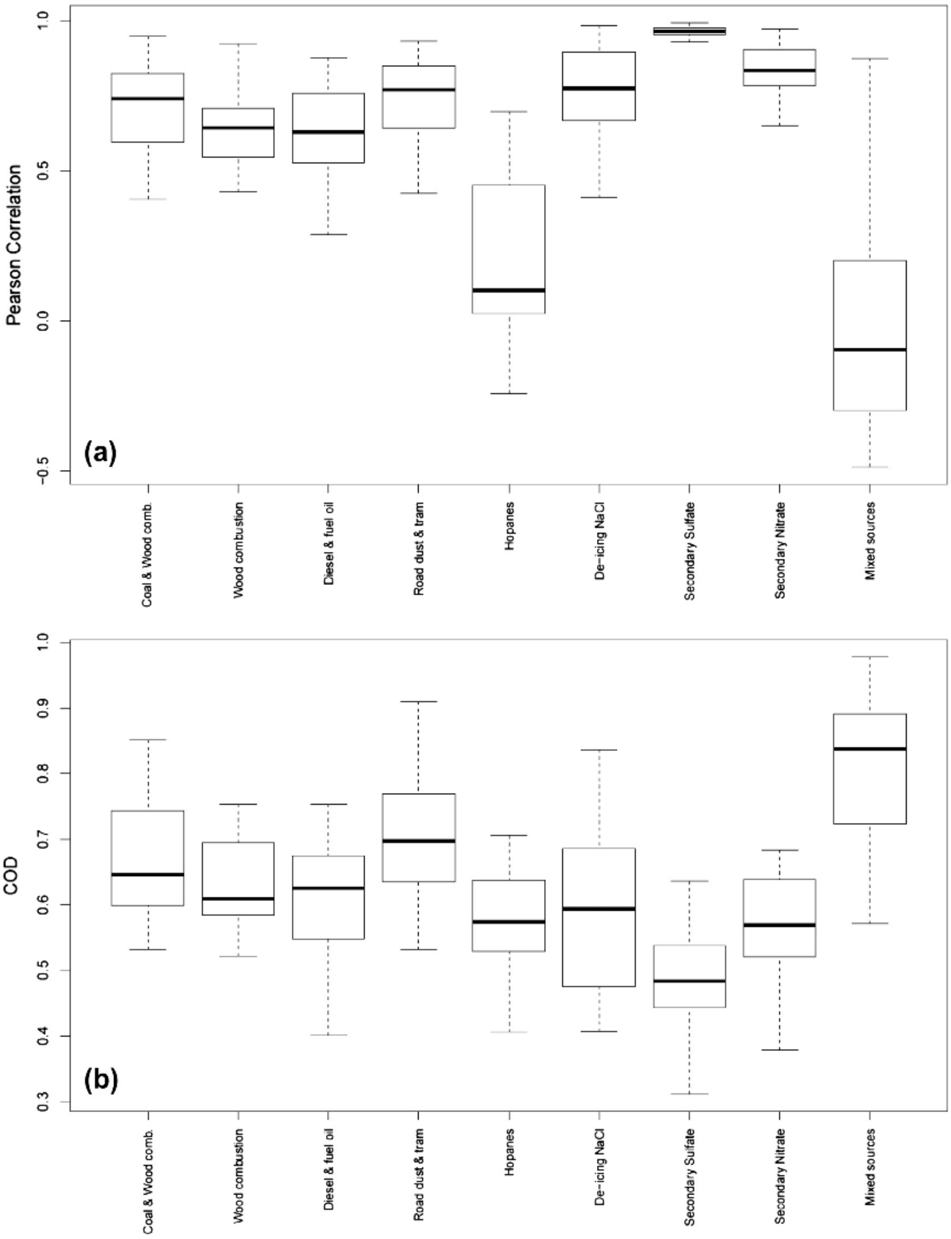


Fig. 5. (a) Pearson correlation coefficients and (b) coefficients of divergence for the nine source factor contributions at eight sampling sites in Augsburg.

different spatiotemporal variation, with a negative median correlation (r) of −0.03 and the highest median COD value of 0.83 between the eight sampling sites. The median correlation coefficient (r) between the KP site and the other sites was approximately −0.07, whereas the other sites exhibited relatively higher correlations between each other. This factor showed a high temporal trend at the KP site during the whole sampling period compared to the other sites. The contribution of factor nine at the KP site was 17-fold higher than the lowest contribution at the KI site (7.0 vs. 0.4 μg m^{-3}).

4. Conclusions

A high correlation among sites does not necessarily indicate uniformity, and particulate source composition is a dominant factor in the determination of spatial variability (Wilson et al., 2005). This study demonstrates that the spatial distributions of source factor contributions can be highly heterogeneous within a given air shed such as city of Augsburg. The results show that heterogeneous spatial variation of source contributions can exist at monitoring sites if there is heterogeneity in the distribution of local sources. In addition, the capability of PMF to resolve the main sources is dependent on the differences in the activities of the various expected sources. When applying PMF, highly correlated emission patterns represent an obstacle for the separation, correct identification and quantification of PM source contributions, specifically when PM variability is predominantly driven by meteorological conditions rather than by the impact of the variability of the emission sources (Gianini et al., 2013). Therefore the PMF might also artificially increase the COD values for the source factor contributions, particularly for species which are distributed between different PMF profiles rather than a particulate profile. For example, the measured inorganic ions (sulfate, nitrate and ammonium ions) showed a very low spatial variation with median COD values of 0.18-0.2 between the eight sampling sites, whereas the corresponding source factor contributions for secondary sulfate and secondary nitrate as separated by PMF showed higher COD values (median of 0.47–0.56) between the eight sampling sites in the city of Augsburg.

Source apportionment was performed using PM_{10} data collected during an intensive one-month sampling campaign in Augsburg, Southern Germany. Samples were collected in parallel at eight sites from February 13 to March 12, 2008. Nine factors were separated by the EPA PMF3.0 model on the basis of the chemical composition of the PM_{10} samples including: POC, water soluble ions, total elements, and carbon fractions (EC/OC). Solid fuel combustion factors (coal & wood combustion; wood combustion), traffic emission-related factors (diesel & fuel oil consumption; road dust & tram; hopanes; de-icing NaCl), secondary inorganic factors (secondary sulfate; secondary nitrate), and a mixed sources (cooking, tobacco smoke and traffic) factor were the main contributors to PM_{10} at the eight sampling sites. The spatiotemporal variation of the source factor contributions was evaluated using the Pearson correlation coefficient (r) and the coefficient of divergence (COD). Secondary sulfate and secondary nitrate were more uniformly distributed (compared to other factors) over the entire study area, as indicated by lower median COD values (0.47 and 0.56) and higher Pearson correlation coefficients ($r = 0.97$ and 0.85), respectively. All factors (except for hopanes and mixed sources) exhibited moderate to high Pearson correlation coefficients between the eight sites and were heterogeneously distributed. In addition to their heterogeneous distribution (COD values of 0.68 and 0.83, respectively), hopanes and the mixed sources factors showed very weak or even negative Pearson correlation coefficients (r) between all sites, indicating that the impact of local source was predominated for both of the hopanes and the mixed sources factors. The coal & wood combustion and wood combustion factors showed very similar levels of contributions at all sites, and showed the maximum contribution at the LfU (urban background) and LSW (residential background) sites, respectively. The diesel & fuel oil consumption, road dust & tram, and hopanes factors exhibited the maximum contribution at the KP, BP, and Bifa sites, respectively. De-icing NaCl and mixed sources factors exhibited the maximum contribution at the KP traffic background site. The average contribution of the secondary sulfate and secondary nitrate factors were very similar at all sites. Again, a high correlation among sites does not necessarily indicate uniformity and the contribution of different sources to the PM_{10} mass at the eight sampling sites indicates that the particle sources were of site-dependent.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.12.015.

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Supplementary Material

Paper: Spatial and temporal variability of source contributions to ambient PM_{10} during winter in Augsburg, Germany using organic and inorganic tracers

Supplementary Material, SM1

Table 2. List of the target analytes Page 1

Chemical species	Abbreviation	KP, ng m-3		BP, ng m-3		LSW, ng m-3		LfU, ng m-3		HT, ng m-3		WE, ng m-3		Bifa, ng m-3		KI, ng m-3	
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Pyrene	PYR	3.4	12.0	2.4	9.0	2.8	8.5	2.5	9.6	1.6	5.9	1.7	5.7	2.5	9.0	2.9	13.8
Fluoranthene	FLU	1.2	4.6	0.7	2.7	0.8	2.3	0.7	2.9	0.4	1.5	0.5	1.5	0.7	2.6	0.8	4.1
Benz[a]anthracene	BAA	1.1	4.2	0.7	3.3	0.8	2.5	0.7	2.7	0.3	1.2	0.4	1.2	0.6	2.2	0.8	3.2
Chrysene	CRY	1.6	4.7	1.4	6.3	1.4	4.1	1.2	4.1	0.6	2.6	0.8	2.1	1.1	3.6	1.4	5.4
Benzo[b,k]fluoranthene	BBKF	1.9	5.6	2.0	7.4	2.0	5.7	1.8	5.7	0.9	3.5	1.3	3.3	1.7	5.0	2.0	5.7
Benz[e]pyrene	BEP	0.6	1.8	0.9	3.0	0.9	2.5	0.8	2.7	0.4	1.3	0.6	1.4	0.7	2.2	1.0	2.4
Benz[a]pyrene	BAP	1.2	4.6	0.8	4.2	1.2	3.8	1.0	3.3	0.4	1.3	0.6	1.6	0.9	3.3	1.1	3.2
9H-Fluoren-9-one	9H-FLU	0.7	3.5	0.2	0.7	0.1	0.8	0.4	1.5	0.1	0.4	0.4	4.4	0.2	0.8	0.1	0.3
Xanthon	XAN	0.7	2.3	0.4	0.9	0.4	1.3	0.5	1.2	0.4	0.9	0.3	0.7	0.3	0.9	0.4	0.8
9,10-Anthracenedione	9,10-ANT	0.3	0.7	0.3	0.7	0.3	0.8	0.3	0.6	0.2	0.5	0.2	0.5	0.3	0.5	0.3	0.5
1,8-Naphthalic anhydride	1,8-NAPH	5.3	20.5	6.9	19.2	5.2	17.1	8.1	25.3	4.7	12.2	4.4	11.0	4.7	21.8	5.7	15.0
Cyclopenta[def]phenanthrenone	CPA	0.1	0.2	0.2	0.6	0.2	0.6	0.2	0.6	0.1	0.3	0.1	0.4	0.1	0.5	0.2	0.6
11H-Benzo[a]fluoren-11-one	11H-BEN	1.2	6.4	0.3	1.0	0.7	3.0	0.3	0.9	0.2	1.0	0.2	0.9	0.3	0.8	0.4	3.7
Bezo[c]fluoren-11-one	BCF	0.5	2.8	0.1	0.4	0.2	0.9	0.1	0.3	0.1	0.3	0.1	0.2	0.1	0.4	0.2	1.4
Benzo[b]fluoren-11-one	BBF	1.3	8.4	0.3	0.8	0.6	2.4	0.3	0.8	0.2	1.0	0.3	0.7	0.3	0.9	0.5	3.9
7H-Benz[de]anthracen-7-one	7H-BEA	8.7	57.3	2.2	9.5	2.9	13.6	1.7	5.3	1.1	4.9	1.7	5.6	2.1	6.0	2.0	7.5
Eicosane	C20	4.9	15.3	0.9	2.9	0.7	2.5	0.5	1.7	0.6	1.3	0.6	1.3	1.0	2.2	1.0	3.2
Heneicosane	C21	3.6	9.4	1.8	5.8	1.3	5.9	1.0	3.0	0.9	3.9	0.7	2.4	1.5	4.1	1.0	2.0
Docosane	C22	5.1	15.0	3.7	13.5	2.2	10.1	1.8	5.5	1.4	7.8	1.4	5.6	3.1	8.7	1.9	4.6
Tricosane	C23	2.4	6.6	3.9	12.7	2.5	10.3	2.0	6.2	1.5	8.5	1.7	6.5	3.3	9.1	2.4	5.4
Tetracosane	C24	5.5	14.6	3.8	11.8	2.9	10.1	2.2	6.3	1.7	8.4	2.2	6.8	3.8	9.3	2.7	5.4
Pentacosane	C25	5.7	15.6	3.0	10.6	2.6	9.7	2.1	6.3	1.5	7.2	1.9	5.5	3.1	8.2	2.3	4.4
Hexacosane	C26	4.3	11.4	5.0	12.2	4.3	11.3	3.5	8.6	2.6	9.5	3.0	6.9	4.6	9.6	4.4	8.7
Heptacosane	C27	3.8	13.6	3.3	8.6	3.9	11.9	2.6	6.1	1.9	8.0	2.0	5.0	2.7	6.4	3.0	5.6
Nonacosane	C29	4.6	13.9	2.7	7.2	2.3	6.8	2.0	5.2	1.4	4.4	1.9	4.0	2.1	4.6	2.1	3.6
Triacontane	C30	2.5	7.7	1.2	3.8	1.2	3.9	1.0	2.5	0.6	2.4	0.8	2.0	1.1	2.3	0.8	2.0
Hentriacontane	C31	4.7	11.6	2.2	7.3	1.9	5.3	1.5	3.7	1.4	3.5	1.2	2.7	1.5	3.0	1.3	2.4
Dotriacontane	C32	1.5	4.2	0.7	2.5	0.6	1.6	0.5	1.6	0.4	1.5	0.4	1.1	0.5	1.0	0.4	1.1
Tritriacontane	C33	2.6	6.6	0.9	2.8	0.8	2.3	0.6	1.4	0.6	1.6	0.3	0.8	0.6	1.2	0.5	1.1

Supplementary Material, SM1

Table 2. List of the target analytes Page 2

Chemical species	Abbreviation	KP, ng m-3		BP, ng m-3		LSW, ng m-3		LfU, ng m-3		HT, ng m-3		WE, ng m-3		Bifa, ng m-3		KI, ng m-3	
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Tetratriacontane	C34	0.8	1.8	0.3	1.1	0.4	2.6	0.3	2.5	0.2	0.6	0.2	0.6	0.2	0.5	0.2	1.0
Pentatriacontane	C35	1.1	2.5	0.2	0.3	0.2	0.4	0.1	0.3	0.1	0.5	0.1	0.3	0.1	0.3	0.1	0.3
Hexatriacontan	C36	0.7	1.8	0.2	0.7	0.2	0.5	0.2	0.7	0.1	0.5	0.1	0.2	0.2	0.4	0.1	0.3
iso- Nonacosane	i-C29	5.6	20.1	0.4	1.0	0.7	3.3	0.3	1.0	0.5	1.5	0.3	1.3	0.4	1.4	1.3	3.1
anteiso- Nonacosane	a-C29	3.2	8.9	0.2	0.4	0.4	1.2	0.1	0.2	0.3	1.0	0.1	0.7	0.1	0.3	0.4	0.8
iso-Triacontane	i-C30	1.5	5.1	0.2	0.4	0.8	2.6	0.1	0.3	0.5	2.1	0.4	1.1	0.1	0.5	0.5	1.9
anteiso-Triacontane	a-C30	3.4	14.2	0.2	0.8	1.0	3.6	0.2	0.5	0.9	2.3	0.3	0.8	0.1	0.3	0.4	1.0
iso-Hentriacontane	i-C31	7.0	19.6	0.2	0.6	1.6	4.0	0.1	0.3	2.0	5.0	0.7	1.8	0.3	0.6	1.1	2.1
anteiso-Hentriacontane	a-C31	1.0	3.3	0.5	2.0	0.4	1.0	0.3	0.9	0.3	0.9	0.1	0.7	0.2	1.0	0.3	2.0
iso-Dotriacontane	i-C32	1.1	3.5	0.2	1.9	0.2	0.8	0.0	0.1	0.2	1.4	0.2	0.6	0.1	0.5	0.2	0.7
anteiso-Dotriacontane	a-C32	5.9	27.2	0.4	1.4	1.6	3.6	0.3	1.4	1.6	3.5	0.8	8.1	0.3	2.5	0.9	1.6
iso-Tritriacontane	i-C33	4.9	15.8	0.2	1.6	1.0	2.6	0.2	0.6	1.0	3.9	0.4	1.4	0.3	1.0	1.0	2.3
anteiso-Tritriacontane	a-C33	0.5	1.8	0.3	0.8	0.1	0.3	0.0	0.2	0.2	1.4	0.1	1.0	0.2	0.7	0.2	1.7
18α(H)-22,29,30-Trisnorhopane	Ts	0.6	1.5	0.3	0.7	0.3	1.6	0.2	0.6	0.1	0.8	0.1	0.3	0.3	0.6	0.3	1.1
17α(H)-22,29,30-Trisnorhopane	Tm	0.7	1.6	0.4	1.0	0.3	0.8	0.3	1.0	0.2	0.9	0.2	0.7	0.3	0.9	0.3	0.7
17 α(H)21β(H)-30-Norhopane	29ab	2.6	6.8	1.3	4.3	1.2	3.9	1.1	3.3	0.8	3.6	0.7	1.9	1.2	2.6	1.1	2.2
17β(H)21α(H)-30-Norhopane	29ba	0.3	1.0	0.3	1.6	0.3	0.9	0.2	0.6	0.1	0.8	0.1	0.4	0.2	0.4	0.2	0.9
17α(H)21β(H)-Hopane	30ab	2.1	6.0	1.2	3.4	1.1	2.5	0.8	2.4	0.7	3.2	0.6	1.3	1.5	2.9	1.1	2.1
17β(H)21α(H)-Hopane (Moretan)	30ba	0.3	1.1	0.2	0.6	0.2	0.8	0.2	0.6	0.1	0.4	0.1	0.4	0.2	0.5	0.2	2.0
22S-17α(H),21β(H)-Homohopane	31abS	0.9	2.3	0.6	1.6	0.9	2.0	0.5	1.5	0.6	2.2	0.4	1.0	0.8	2.0	1.2	4.9
22R17α(H),21β(H)-Homohopane	31abR	1.1	4.9	0.9	3.1	1.1	4.3	0.7	2.2	0.6	1.8	0.4	1.3	1.1	2.7	0.9	3.4
22S-17α(H),21β(H)-Bishomohopane	32abS	0.5	1.3	0.3	1.0	0.2	0.7	0.2	0.7	0.2	0.8	0.2	0.7	0.4	0.9	0.5	3.1
22R-17α(H),21β(H)-Bishomohopane	32abR	0.3	0.9	0.2	0.6	0.2	0.7	0.2	0.5	0.2	0.7	0.1	0.4	0.3	0.7	0.5	3.9
Cholesterol	CHO	0.9	2.3	0.0	0.0	0.2	2.1	0.0	0.0	0.4	7.6	0.2	1.0	0.0	0.4	0.3	2.0
Palmitic acid	PAL	187	270	71	160	60	110	59	126	51	102	56	129	53	279	83	154
Linoleic acid	LIN	0.5	2.0	0.2	5.1	5.3	15.2	1.1	17.9	4.2	16.5	4.3	13.5	8.4	79.7	5.5	24.0
Oleic acid	OLE	1.4	4.5	0.1	1.6	2.0	4.8	0.4	5.5	1.7	7.7	1.6	4.3	2.8	25.5	2.2	8.6
Stearic acid	STE	109	194	26	65	37	58	25	58	31	59	32	61	20	116	42	102

Supplementary Material, SM1

Table 2. List of the target analytes Page 3

Chemical species	Abbreviation	KP, ng m-3		BP, ng m-3		LSW, ng m-3		LfU, ng m-3		HT, ng m-3		WE, ng m-3		Bifa, ng m-3		KI, ng m-3	
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Dehydroabietic acid methylester	DHAA-ME	14.6	42.2	8.1	57.6	8.8	21.2	12.4	66.6	2.5	6.2	4.8	23.1	7.2	48.2	10.2	33.6
Dehydroabietic acid (tms)	DHAA	181	708	6	70	125	397	5	100	36	114	68	241	25	204	72	225
Levoglucosan	LEVO	353	945	274	821	437	1109	273	859	197	596	308	755	280	812	361	770
Arsenic	As	0.8	4.2	0.6	3.4	0.7	6.9	0.7	5.3	0.4	2.8	0.5	3.3	0.6	1.9	0.6	1.7
Calcium	Ca	1108	2301	461	1335	340	854	528	2036	193	594	229	617	383	1285	288	935
Cadmium	Cd	0.2	0.7	0.2	0.6	0.2	0.7	0.2	0.6	0.1	0.7	0.1	0.4	0.2	0.6	0.2	0.4
Cerium	Ce	0.5	1.0	0.2	0.7	0.2	0.3	0.2	0.5	0.1	0.3	0.1	0.3	0.2	0.4	0.2	0.5
Cobalt	Co	0.3	0.7	0.1	0.9	0.1	1.0	0.1	0.5	0.2	3.4	0.1	0.6	0.1	0.5	0.1	0.4
Chromium	Cr	12.3	24.1	3.2	9.4	1.8	5.8	2.0	6.3	1.5	1.5	1.5	1.5	1.8	4.7	1.5	1.5
Cupper	Cu	56.3	126.2	20.3	65.1	12.0	31.8	13.1	40.4	5.6	15.4	6.0	14.6	12.9	33.0	10.2	26.1
Iron	Fe	1823	3728	578	2014	314	966	327	1049	166	461	158	405	367	1036	321	992
Potassium	K	251	615	234	606	226	593	221	547	171	524	190	367	234	495	237	425
Lanthanum	La	0.3	0.6	0.2	0.4	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.2	0.1	0.3	0.1	0.3
Magnesium	Mg	266.1	490.6	130.2	335.6	103.9	226.5	109.0	267.5	81.4	201.7	84.7	173.8	115.5	330.7	79.1	247.1
Manganese	Mn	25.3	48.1	9.9	30.8	6.7	23.4	7.4	23.1	4.7	12.6	4.6	17.1	9.2	25.0	9.9	48.2
Nickel	Ni	5.7	12.2	1.5	4.6	0.9	3.1	0.9	2.4	0.7	1.7	0.6	1.2	0.8	1.9	1.1	8.2
Lead	Pb	7.6	21.9	6.7	19.9	5.8	22.9	5.7	17.5	4.6	22.9	4.3	11.3	6.4	21.0	4.8	10.6
Antimony	Sb	7.4	16.3	2.8	9.1	1.7	4.4	1.8	5.3	0.9	2.6	0.9	2.0	1.9	5.0	1.4	3.5
Titanium	Ti	5.7	11.3	3.4	8.2	2.9	7.3	5.3	66.4	2.4	6.3	2.7	6.4	3.2	7.0	3.0	7.0
Zinc	Zn	66.8	216.2	42.8	231.6	41.9	190.4	32.4	89.4	26.1	99.2	28.6	209.7	38.6	130.8	33.5	86.4
Chloride	Cl^-	1836	10377	756	3037	594	1764	585	1880	508	1717	500	1795	688	2773	394	1156
Nitrate	NO_3^-	6770	22111	6654	22072	6231	21310	6420	20043	6730	21992	5625	14751	6683	20213	6078	14558
Sulfate	SO_4^{-2}	2285	9931	2217	8928	2454	10148	2252	9221	1971	8747	1811	7168	2330	10426	1999	7662
Ammonium	NH_4^+	2515	9697	2536	10111	2545	10410	2478	9403	2580	10333	2217	7346	2678	10167	2390	7060
Sodium	Na^+	1190	6457	556	1842	418	1254	411	1283	372	1222	350	1220	452	1778	245	960
Elemental carbon	EC	4440	9135	2672	7881	2276	8174	2319	6366	1333	5493	1513	4380	2312	6406	1901	3789
Organic carbon	OC	4182	9465	3237	9205	3025	10682	3146	9431	2200	9470	2356	5834	3162	7998	2960	7110

Supplementary Material, SM2

PMF sensitivity

A sensitivity analysis of the PMF model was performed to examine the impact of the number of factors selected for the PMF computation with most reasonable interpretation. Varied numbers from 6 to10 of PMF factors were examined to assess the consistency of the PMF solution with the current understanding of the source profiles. The 6-factor solution produced a factor dominated with 80% of levoglucosan, potassium, hopanes, PAH and O-PAH. A second factor was separated and dominated mainly by secondary inorganics (nitrate, sulfate and ammonium). A third factor was characterized with about 80% of both Na^+ and Cl^-. For factor 4, n-alkanes, iso & anteiso-alkanes, hopanes and fatty acids were the main contributors. Factor 5 was associated with high elemental concentrations about 60% of each of Ca, Cr, Fe and Cu. In addition more than 30% of EC was associated too in this factor. The last factor was dominated by more than 50% of hopanes and up to 40% of n-alkanes (C_{20}-C_{26}).

By increasing the number of factors to seven, the first factor in the 6-factor solution was split into two factors: one dominated by levoglucosan (about 70%), potassium, PAH and O-PAH and contributing approximately 25% of OC fraction, while the other factor was dominated by hopanes and the rest of levoglucosan, PAH and O-PAH. The other five factors remained greatly unchanged. The 8-factor solution produced an additional factor characterized mainly by n-alkanes (C_{20}-C_{25}) and some hopanes, while the 9-factor solution separates the factor of secondary inorganic aerosol components into two factors, secondary nitrate and secondary sulfate. On the other hand, the 10-factor solution leads to splitting one of the factors of the 9-factor solution with no more reasonable interpretation and therefore has been rejected accordingly.

In our study, altering the Fpeak value was not found to result in substantially better source profiles. Consequently, base run results (Fpeak = 0) are reported in this paper. In order to compare the results from run to run, a total of 100 random runs with minimum correlation R-value of 0.6 were computed for each data set to ensure no local minima of Q values were observed.. The convergent run with the Q value closest to the target Q value was used as the base run. Then 100 bootstrap runs were performed to assess the uncertainty of the factor loadings and factor scores in the base run.

Besides routine bootstrap model runs, which showed good stability, the stability of the nine factors at all sampling sites has been examined in two additional analyses. Firstly the pre- and post-three-month sampling data from KP site were included in the PMF analysis. No significant effect was noticed on the factor profiles or on the factor contributions for the nine factors at all sampling sites. Secondly, the PMF analyses have been performed through excluding data from one of the sites from the PMF inputs in sequence and respectively. Subsequently, the PMF runs were performed with data from seven different sites in this test. Again, there was no significant effect of one of the sites on the stability of the nine factors at other sites except when KP data were excluded. The effect was obvious on the profiles and contributions of the four traffic related factors and the mixed sources factor as well.

In the table below (Table 3a&b), the categories of the species for PMF analysis are illustrated.

Supplementary Material, SM2

Table 3 a. Chemical species with categories (WEAK and STRONG) for the PMF analysis

Chemical species	PMF Category	Chemical species	PMF Category	Chemical species	PMF Category
Pyrene (PYR)	WEAK	Tritriacontane (C33)	STRONG	Stearic acid (STE)	WEAK
Fluoranthene (FLU)	WEAK	Tetratriacontane (C34)	WEAK	Dehydroabietic acid methylester (DHAA-ME)	WEAK
Benz[a]anthracene (BAA)	WEAK	Pentatriacontane (C35)	WEAK	Dehydroabietic acid (tms) (DHAA)	WEAK
Chrysene (CRY)	WEAK	Hexatriacontan (C36)	WEAK	Levoglucosan (LEVO)	STRONG
Benzo[b,k]fluoranthene (BBKF)	WEAK	iso- Nonacosane(i-C29)	WEAK	Arsenic (As)	STRONG
Benz[e]pyrene (BEP)	WEAK	anteiso- Nonacosane (a-C29)	WEAK	Calcium(Ca)	WEAK
Benz[a]pyrene (BAP)	WEAK	iso-Triacontane (i-C30)	WEAK	Cadmium(Cd)	STRONG
9H-Fluoren-9-one (9H-FLU)	WEAK	anteiso-Triacontane (a-C30)	WEAK	Cerium(Ce)	STRONG
Xanthon (XAN)	WEAK	iso-Hentriacontane (i-C31)	WEAK	Cobalt (Co)	WEAK
9,10-Anthracenedione (9,10-ANT)	WEAK	anteiso-Hentriacontane (a-C31)	WEAK	Chromium (Cr)	WEAK
1,8-Naphthalic anhydride (1,8-NAPH)	WEAK	iso-Dotriacontane (i-C32)	WEAK	Cupper (Cu)	STRONG
Cyclopenta[def]phenanthrenone (CPA)	WEAK	anteiso-Dotriacontane (a-C32)	WEAK	Iron (Fe)	STRONG
11H-Benzo[a]fluoren-11-one (11H-BEN)	WEAK	iso-Tritriacontane (i-C33)	WEAK	Potassium (K)	STRONG
Bezo[c]fluoren-11-one (BCF)	WEAK	anteiso-Tritriacontane (a-C33)	WEAK	Lanthanum (La)	WEAK
Benzo[b]fluoren-11-one (BBF)	WEAK	18α(H)-22,29,30-Trisnorhopane (Ts)	WEAK	Magnesium (Mg)	WEAK
7H-Benz[de]anthracen-7-one (7H-BEA)	WEAK	17α(H)-22,29,30-Trisnorhopane (Tm)	WEAK	Manganese (Mn)	STRONG
Eicosane (C20)	WEAK	17 α(H)21β(H)-30-Norhopane (29ab)	STRONG	Nickel (Ni)	WEAK
Heneicosane (C21)	WEAK	17β(H)21α(H)-30-Norhopane (29ba)	STRONG	Lead (Pb)	WEAK
Docosane (C22)	STRONG	17α(H)21β(H)-Hopane (30ab)	STRONG	Antimony (Sb)	STRONG
Tricosane (C23)	STRONG	17β(H)21α(H)-Hopane (Moretan) (30ba)	STRONG	Titanium (Ti)	STRONG
Tetracosane (C24)	STRONG	22S-17α(H),21β(H)-Homohopane (31abS)	WEAK	Zinc (Zn)	STRONG
Pentacosane (C25)	STRONG	22R17α(H),21β(H)-Homohopane (31abR)	WEAK	Chloride (Cl-)	STRONG
Hexacosane (C26)	STRONG	22S-17α(H),21β(H)-Bishomohopane (32abS)	WEAK	Nitrate (NO3-)	STRONG
Heptacosane (C27)	STRONG	22R-17α(H),21β(H)-Bishomohopane (32abR)	WEAK	Sulfate (SO4-2)	STRONG
Nonacosane (C29)	STRONG	Cholesterol (CHO)	WEAK	Ammonium (NH4+)	STRONG
Triacontane (C30)	STRONG	Palmitic acid (PAL)	WEAK	Sodium (Na+)	STRONG
Hentriacontane (C31)	STRONG	Linoleic acid (LIN)	WEAK	Elemental carbon (EC)	STRONG
Dotriacontane (C32)	STRONG	Oleic acid (OLE)	WEAK	Organic carbon (OC)	STRONG

Table 3 b. Chemical species with categories (BAD) for the PMF analysis

Chemical species	PMF Category	Chemical species	PMF Category
Phenanthrene (PHE)	BAD	Hexadecanoic acid, methyl ester (HEA)	BAD
Anthracene (ANT)	BAD	Octadecanoic acid, methyl ester (OCA)	BAD
Perylene (PER)	BAD	Isopimaric acid (ISA)	BAD
Dibenz[ah]anthracene (DAH)	BAD	Abietic acid (AA)	BAD
Indeno[1,2,3-cd]pyrene (IND)	BAD	Mannosan (MAN)	BAD
Picene (PIC)	BAD	Vanillin (VAN)	BAD
Benzo[ghi]perylene (BGH)	BAD	Vanillic acid (tms) (VAA)	BAD
Coronene (COR)	BAD	Acetosyringone (ASY)	BAD
Nonadecane (C19)	BAD	Syringic acid (SYA)	BAD
17β(H)-22,29,30-Trisnorhopane (27b)	BAD	Thallium (Tl)	BAD

Supplementary Material, SM3

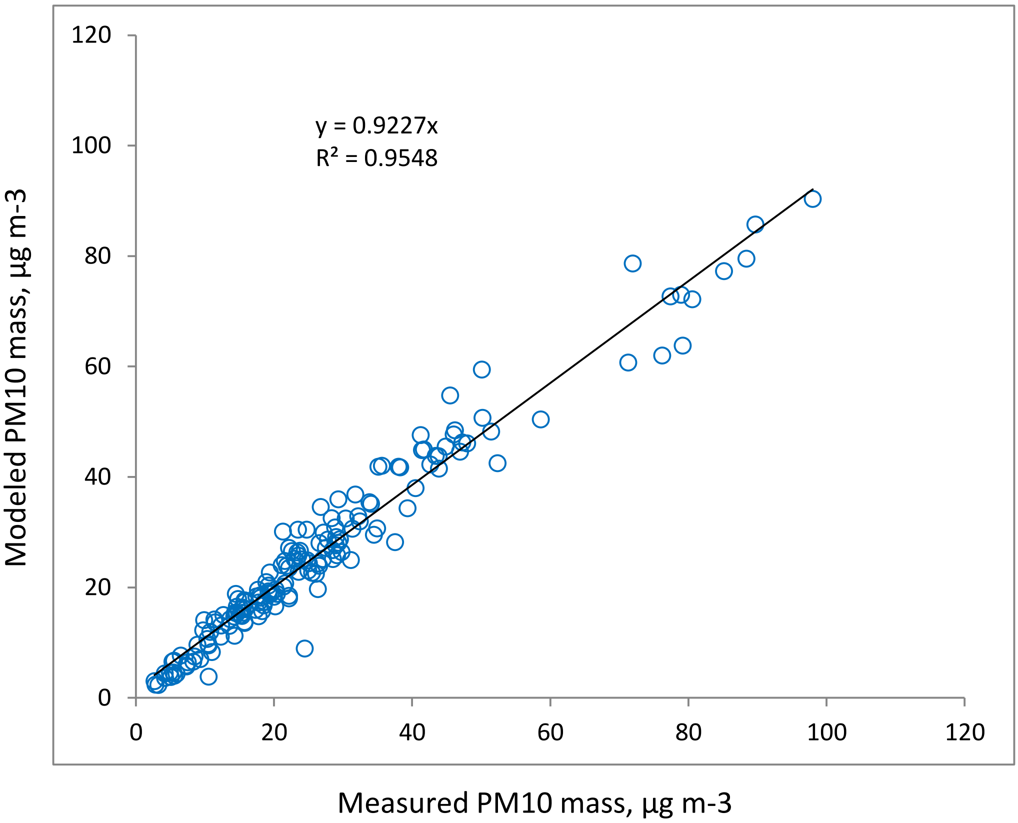

Figure: Linear regression of PM_{10} mass between measured and PMF modeled results at six sampling sites in February 13 – March 12, 2008. Note that PM_{10} mass concentrations were not measured at the LSW and HT sites. The modeled PM_{10} is calculated as a sum of 9 factors.

The mean modeled PM_{10} mass concentrations are in good agreement with the measured PM_{10}, as shown in the following table.

Table: Mean PM_{10} mass between measured and PMF modeled results

µg m^{-3}	KP	BP	LSW	LfU	HT	WE	Bifa	KI
PM_{10} measured	42.7	28.0	NA	24.6	NA	17.6	26.1	19.0
PM_{10} modeled	43.3	27.1	24.5	23.8	18.7	18.4	24.8	20.3

Supplementary Material, SM4

Table 4a. Median of Pearson correlation coefficients (r) for the nine source factor contribution between the eight sampling sites

Factors	KP	BP	LSW	LfU	HT	WE	Bifa	KI
Factor 1: Coal & Wood combustion	0.80	0.85	0.79	0.83	0.65	0.75	0.85	0.62
Factor 2: Wood combustion	0.61	0.66	0.73	0.69	0.61	0.59	0.71	0.66
Factor 3: Diesel & fuel oil consumption	0.75	0.77	0.51	0.77	0.58	0.76	0.64	0.68
Factor 4: Road dust & tram	0.70	0.71	0.80	0.84	0.73	0.54	0.79	0.83
Factor 5: Hopanes	0.10	0.44	0.42	0.38	0.53	-0.01	0.40	0.07
Factor 6: De-icing NaCl	0.47	0.78	0.97	0.90	0.85	0.84	0.81	0.69
Factor 7: Secondary sulfate	0.97	0.98	0.97	0.98	0.97	0.96	0.97	0.96
Factor 8: Secondary nitrate	0.88	0.90	0.83	0.86	0.79	0.90	0.87	0.78
Factor 9: Mixed sources	-0.07	-0.06	0.15	-0.06	-0.03	-0.09	-0.03	-0.01

Table 4b. Median of Coefficient of Divergence (COD) for the nine source factor contributions between the eight sampling sites

Factors	KP	BP	LSW	LfU	HT	WE	Bifa	KI
Factor 1: Coal & Wood combustion	0.63	0.59	0.65	0.62	0.75	0.64	0.61	0.69
Factor 2: Wood combustion	0.60	0.59	0.67	0.58	0.63	0.59	0.59	0.72
Factor 3: Diesel & fuel oil consumption	0.54	0.58	0.67	0.55	0.68	0.58	0.61	0.62
Factor 4: Road dust & tram	0.76	0.62	0.68	0.65	0.67	0.74	0.66	0.73
Factor 5: Hopanes	0.58	0.51	0.65	0.49	0.52	0.56	0.53	0.63
Factor 6: De-icing NaCl	0.66	0.52	0.58	0.45	0.47	0.56	0.51	0.71
Factor 7: Secondary sulfate	0.48	0.43	0.50	0.44	0.44	0.48	0.47	0.55
Factor 8: Secondary nitrate	0.61	0.52	0.63	0.59	0.56	0.53	0.46	0.55
Factor 9: Mixed sources	0.88	0.86	0.76	0.83	0.73	0.83	0.84	0.83

PUBLICATION 2

Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany

by

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Raeed Megeed Qadir was responsible for the laboratory analysis of organic compounds and instrumental maintenance. He also performed the positive matrix factorization (PMF) analysis, processed all data sets and wrote the paper. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

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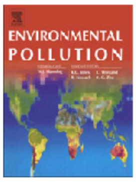

Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany

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ABSTRACT

Within the Munich low emission zone (LEZ), samples of $PM_{2.5}$ were collected before (2006/2007) and after (2009/2010) the implementation of the LEZ. The samples were analyzed for carbon fraction (EC/OC) and particulate organic compounds (POC). Significant lower concentrations were noticed for elemental carbon (EC) and some of the POC like vanillic acid, acetosyringone, syringylacetone and syringic acid after the implementation of the LEZ. Higher concentrations of levoglucosan, retene and O-PAH were detected in the second sampling period. Positive matrix factorization (PMF) was used to identify the main sources of POC. Emissions from traffic, solid fuels combustion, cooking and mixed source were separated. The contribution of traffic source factor was decreased about 60% after the implementation of the LEZ. Thus the average concentration of EC from traffic factor decreased from 1.1 to 0.5 μg/m^3 after the implementation of the LEZ.

1. Introduction

The chemical composition of ambient particulate matter (PM) varies considerably and consists of many different compounds (Tsigaridis et al., 2006). Aerosol carbon is commonly classified as organic carbon (OC) and elemental carbon (EC). OC can be directly emitted to the atmosphere in the particulate form (primary organic aerosol) or can be produced by gas-to-particle conversion processes (secondary organic aerosol). EC is emitted from combustion sources (Cabada et al., 2004). The organic constituents of airborne particles influence the behavior and impact of PM on human health, regional visibility and global climate (NRC, 1999). Organic compounds of biogenic and anthropogenic origin often represent a large fraction, up to 40%, of total PM mass (Chow et al., 2006). The concentrations of organic compounds ranging from below pg/m^3 to μg/m^3 (Tsapakis et al., 2002). Knowledge of the temporal and spatial variation of particulate organic matter (POM) and its chemical composition are clearly needed to understand its climate and adverse human health effects (Fuzzi et al., 2006). To protect both human health and the environment, it is important to combat pollutant emissions at the source and identify and implement the most effective reduction measures at local, national and international levels. Comprehensive studies are therefore necessary to evaluate the characteristics of PM at the different sources (Aldabe et al., 2011). Organic compounds have been used as source indicators in aerosol research for many years and several studies have used organic compounds for source apportionment (Cass, 1998; Schauer et al., 1998; Schnelle-Kreis et al., 2007). Positive matrix factorization (PMF), an advanced receptor models, has been successfully used for quantitative identification of sources of organic pollutants in aerosols by several researchers (Shrivastava et al., 2007; Song et al., 2007; Uchimiya et al., 2007). PMF rotates the matrices of factor loadings and scores with positive constraints, which makes factor axes less orthogonal and makes factor loadings and factor scores more interpretable (Paatero and Tapper, 1994).

Low Emission Zones (LEZ) are areas in which vehicular traffic access is restricted to vehicles that emit only low levels of air pollutants only. The most severe environmental problems in Munich are caused by traffic. Vehicles with internal combustion engines contribute significantly to air pollution. Their exhaust contains pollutants such as particulate matter (PM_{10}) and nitrogen dioxide (NO_2). The ultrafine particles of particulate matter can penetrate into the lungs and pass through the alveoli into the bloodstream.

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Possible symptoms are respiratory diseases and cardiovascular system. To improve the air quality and protect human health, many German cities have introduced environmental zones. The principle is to get rid of the bad source of emissions from the city center and to reduce the extremely high volume of traffic, which makes the ventilation very poor. Many heavy duty vehicles made their way through the city of Munich until February 2008 when the pre-stage of LEZ implementation was started by preventing the heavy duty vehicles from going through the city center. Later in October 2008, a LEZ was established in the inner city in order to pursue the reduction of pollution. The first stage of LEZ allowed vehicles with emission requirement of Euro2, Euro3 and Euro4 (http://www.dieselnet.com/standards/eu/ld.php) only to enter the inner city. The second stage of LEZ started in October 2010, allowing vehicles with emission requirement Euro3 and Euro4 only to go through the LEZ area. The final stage will start in October 2012 and will allow only the vehicles with Euro4 emission requirements to access the LEZ area (RGU, 2012).

In the light of what is mentioned above, the main aim of this study is to assess the effect of the implementation of LEZ on both concentrations and source contribution of the POC. This has been accomplished through depending on the chemical characterization of the particulate fraction of organic PM and identifying sources of the POC. EPA-PMF 3.0 model has been chosen as a receptor-based model for the source apportionment. Thus, chemical composition of $PM_{2.5}$ samples collected over two different periods, before LEZ implementation (2006–2007) and after LEZ implementation (2009–2010) have been used in order to estimate the POC sources and their contributions.

2. Material and methods

2.1. PM sampling

The sampler for $PM_{2.5}$ was located at the monitoring site in Lothstrasse (latitude 48° 9′16″N; longitude 11° 33′17″E). This site is part of the air hygienic monitoring system of Bavaria consisting of more than 50 monitoring stations in the whole of Bavaria. It is conducted by the Bavarian State Office for Environment (Bayerisches Landesamt für Umwelt, BLfU). Lothstrasse is situated in the inner city of Munich near to a main road. It is a traffic influenced station with approximately 41 000 passing vehicles per day. Moreover, the local area is mainly composed of habitation, trade and commerce (BSUGV, 2004) (Fig. 1).

Ambient samples were collected every third day from October 2006 to February 2007 and from October 2009 to February 2010 (Fig. 2). Total of 82 samples were collected during these two periods before and after the implementation of the LEZ. Prior to sampling, quartz fiber filters were baked for at least 12 h in a circulating air oven from Nabertherm (Lilienthal, Germany) at 500 °C to remove all organic matter.

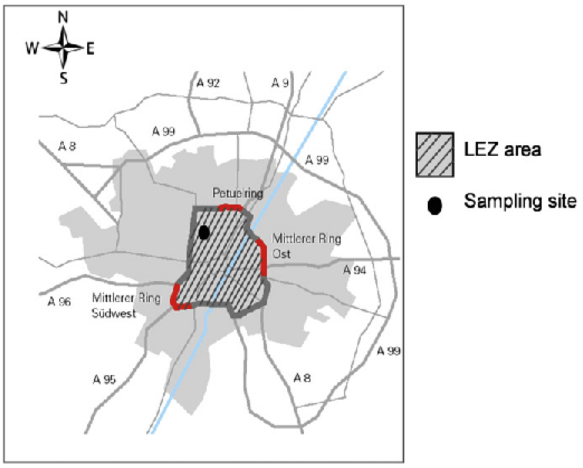

Fig. 1. Location of the sampling site in Munich.

For chemical analysis, $PM_{2.5}$ samples were collected with high volume sampler (Model GS2310 Series, Andersen Instruments Inc., Georgia, USA) on 203 mm × 254 mm (loaded area is 180 mm × 230 mm) quartz fiber filters (Whatman International Ltd., Maidstone, England) at a flow of 1 m^3/min for 24 h. The samples were stored in glass containers at −18 °C until analysis.

2.2. Chemical analysis

The samples were analyzed for POC by using in-situ derivatization thermal desorption gas chromatography time of flight mass spectrometry (IDTD-GC-ToF-MS) method (Orasche et al., 2011). The method allows derivatization using N-Methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) reagent of the polar organic fraction of filter samples in-situ on the filter during thermal desorption. Derivatization and desorption of polar organic compounds occurs directly from particulate matter on the filters. The advantages of employing the direct thermal desorption system employed for this study are: (1) direct placement of samples in the GC liner, so called in-injector thermal desorption avoiding sample transfer lines frequently causing cold spots, (2) the possibility of automatic liner exchange, (3) rapid heating rates of the injector and (4) replacement of the GC liner for every sample.

The other details of the IDTD-GC-ToF-MS method and sample preparation were described by Orasche et al. (2011). Elemental and organic carbon fraction (EC and OC) were analyzed by thermal-optical analysis (IMPROVE-A protocol) (Chow et al., 2007) in cooperation with the Desert Research Institute (DRI), Nevada, USA.

2.3. Statistical treatment of data

All data processing and descriptive statistics for the two sampling periods were performed with a level of significance of ($\alpha = 0.05$). The MedCalc v.12.2.1.0 program (MedCalc Software, Broekstraat 52, 9030 Mariakerke, Belgium) was used for all statistical procedures. The first test was the detection of the outliers. The statistical test that was performed detected seven days with very high outlier values of POC especially hopanes and n-alkanes in the second sampling period in 2009/10. According to the information provided by the state building authorities in Munich (Staatliches Bauamt München, SBM in German), there was construction activity at the building of Munich Technical College of Engineering, Automotive Engineering and Aviation Technology (Dachauer Strasse 98b) during the second sampling period in 2009/10 and near the sampling site. Use of lorries and big trucks during the construction were the possible sources of high concentration of hopanes and n-alkanes in those seven days. The data obtained from those seven days were excluded from further data analysis. Statistical *t-test* was performed to compare the concentration of each of the POC between the two sampling periods.

2.4. Positive matrix factorization

Positive Matrix Factorization (PMF) is a multivariate tool that decomposes a matrix of data samples into two sub-matrices, the factor profiles and factor contributions (EPA, 2008). It was developed by Paatero (1997, 1999) and was employed to resolve dominant positive factors on the basis of observation without detailed prior knowledge of the sources and source profiles. The model used in this study was EPA-PMF 3.0, developed by U.S. EPA based on the ME-2 algorithm.

A total of 78 POC for each sample were measured, but only 67 selected organic species were used for the PMF analysis beside the EC and OC. The selected species represents: polycyclic aromatic hydrocarbons (PAH), oxidized polycyclic aromatic hydrocarbons (O-PAH), n-alkanes, iso & anteiso alkanes, hopanes, resin acids, fatty acids, anhydrous sugars and phenolic compounds. The organic species with more than 33% of values under the limit of quantification (LOQ) have been excluded from the PMF input. The error fractions were increased up to 20% for each of the organic species with 10–33% of values under the LOQ. Data lower than the LOQ were replaced by half of the LOQ and their uncertainties were set to five-sixths of the LOQ (Polissar et al., 1998) with no missing data. The uncertainties of the other values were calculated according to Norris et al. (2008) in the following equation:

$$u = \left[(\text{Error fraction} \times \text{Concentration}) + (\text{LOQ})^2\right]^{0.5}$$

Error fraction is the percentage of uncertainty and estimated from sampling error and analytical errors consequently. PMF analyses were run with three to six factors in order to find the most reliable and best interpretable results.

3. Results and discussions

3.1. Characterization and concentrations of POC

Table 1 gives a summary of ambient concentrations of 78 POC, EC and OC. The results indicated that mean concentrations for most of the PAH after implementation of the LEZ were slightly but not significantly ($P > 0.05$) decreased. Retene which is considered as

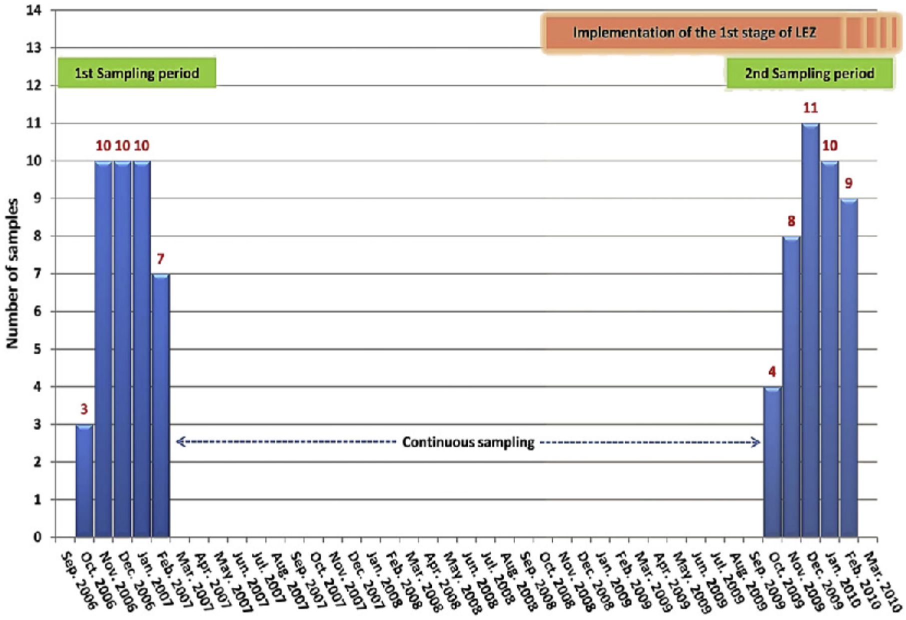

Fig. 2. Time line of the number of samples and sampling in both periods.

a marker for coniferous wood combustion (Simoneit et al., 2000) showed a significant difference ($P < 0.05$) with higher mean concentration of 0.25 ng/m^3 after the implementation of LEZ compared with 0.14 ng/m^3 before implementation of LEZ.

Fig. 3 shows the time series of EC and some other selected POC. Significantly higher concentrations of most of the O-PAH were detected in the second sampling period 2009/10. O-PAH have been identified in source samples from gasoline, diesel, coal, wood, and municipal waste combustion. Photo oxidation of PAH has also been found to produce O-PAH (Allen, 1997). Like for retene, significant higher concentration of levoglucosan was noticed in the second sampling period after the implementation of LEZ. The O-PAH, levoglucosan and retene were observable with higher concentrations in 2009/10, which are considered to be markers for wood combustion (Schauer et al., 2001; Simoneit et al., 2000; Sklorz et al., 2007) This may be due to the colder winter scenario in 2009/10 compared with 2006/07 and the trend of an increasing use of wood burning for household heating in Germany (Cocchi, 2011). Depending on the meteorological information provided by BLfU, the temperature in winter 2009/10 ranged from −10 to 14 °C while ranged from −7 to 22 °C in winter 2006/07. Although the use of wood for domestic heating is very familiar to the general public especially in the countryside (Bari et al., 2011) nevertheless, urban areas are also impacted from local wood combustion (Brandt et al., 2011). A lower concentration of EC with significant difference ($P < 0.05$) was detected after the implementation of LEZ in 2009/10. EC is regarded as an indicator for traffic emission (Baccarelli et al., 2011; Sonntag et al., 2012), for showing to some extent a positive effect of LEZ implementation. The concentrations of phenolic compounds were also decreased significantly ($P < 0.05$) in the second sampling period.

The presence of hopane biomarkers in aerosols confirms an input source from fossil fuel utilization (i.e. mainly vehicular traffic) (Simoneit, 2002). No significant differences ($P > 0.05$) in the concentrations of any of hopanes were detected before and after the implementation of LEZ, but like for the PAH slightly lower concentrations were found in 2009/10. Also no significant differences ($P > 0.05$) were noticed in the concentrations of the other measured POC or OC.

3.2. PMF results

3.2.1. PMF sensitivity and implementation

PMF results depend on the number of factors included in the model and the amount of rotation imposed on the solution. Interpretability was the key basis for judging the optimum values for these parameters. Interpretable solutions were those that grouped source-class-specific sets of markers into distinct factors. Models that grouped markers for multiple source classes into the same factor, distributed markers for one source class across multiple factors, or contained factors with no distinctive groupings of compounds were judged less interpretable and rejected. While no molecular marker pattern can be unambiguously associated with a specific source class, this approach provides a systematic basis for sorting through the possible PMF models (Shrivastava et al., 2007).

The EPA-PMF 3.0 model also provides the rotational freedom parameter (Fpeak) function that can control whether more extreme values are assumed for the factor loadings (by assigning positive Fpeak values) or the factor scores (by assigning negative Fpeak values). In our study, altering the Fpeak value was not found to result in substantially better source profiles. Consequently, base run results (Fpeak = 0) are reported in this paper. In order to compare the results from run to run, a total of 100 random runs with minimum correlation R-value of 0.6 were computed for each data set to ensure no local minima of Q values were observed. The convergent run with the Q value closest to the target Q value was used as the base run. Then 100 bootstrap runs were performed to assess the uncertainty of the factor loadings and factor scores in the base run.

The abnormal seven days of the second sampling period mentioned before were excluded from the PMF runs. A different factor number between 3 and 6 was tested to find out the most reliable PMF method. As described in the PM sampling, traffic is one of the

Table 1
Statistical summary of POC concentrations (ng m^{-3}), EC and OC concentrations ($\mu\text{g m}^{-3}$).

Substance	Abbreviation	Before LEZ (2006–2007), $n = 40$				After LEZ (2009–2010), $n = 35$			% < LOQ	*t*-Test (*P* value)
		LOQ	Mean	Median	Range	Mean	Median	Range		
PAH										
Benz[a]anthracene	BAA	0.02	0.50	0.33	0.05–2.30	0.43	0.28	0.07–3.00	0	0.51
Chrysene	CRY	0.02	1.44	0.94	0.20–6.50	1.28	0.83	0.30–9.00	0	0.85
Benzo[x]fluoranthene	BBKF	0.04	1.99	1.64	0.26–7.90	1.75	1.17	0.30–10.50	0	0.58
Benz[e]pyrene	BEP	0.04	0.64	0.45	0.09–2.50	0.52	0.35	0.10–3.10	1	0.52
Benz[a]pyrene	BAP	0.04	0.84	0.56	0.08–3.90	0.70	0.40	0.10–4.80	1	0.41
Perylene	PER	0.02	0.10	0.08	0.01–0.40	0.09	0.06	0.01–0.50	3	0.50
Dibenz[ah]anthracene	DAH	0.02	0.15	0.09	0.01–0.60	0.13	0.08	0.02–0.70	8	0.56
Indeno[1,2,3-cd]pyrene	IND	0.05	1.09	0.71	0.13–5.30	0.84	0.59	0.16–4.60	1	0.30
Picene	PIC	0.05	0.16	0.10	0.02–0.70	0.15	0.09	0.02–1.00	21	0.90
Benzo[ghi]perylene	BGH	0.05	1.08	0.76	0.15–4.50	0.75	0.45	0.15–4.30	1	0.15
Coronene	COR	0.10	0.52	0.48	0.24–1.20	0.45	0.43	0.20–0.80	4	0.08
Retene	RET	0.10	0.14	0.10	0.01–0.60	0.25	0.17	0.03–1.00	1	**0.03**
Oxidized PAH										
9H-Fluoren-9-one	9H-FLU	0.02	0.28	0.21	0.06–0.90	0.57	0.39	0.03–2.30	0	**0.01**
Xanthon	XANT	0.02	0.18	0.17	0.02–0.50	0.15	0.10	0.03–1.00	0	0.20
9,10-Anthracenedione	9,10-ANT	0.02	1.34	1.19	0.32–3.60	2.52	1.78	0.40–11.80	0	**0.01**
1,8-Naphthalic anhydride	1,8-NPA	0.10	1.17	1.01	0.15–4.90	2.39	1.47	0.40–10.60	0	**0.01**
Cyclopenta[def]phenanthrenone	CPPH	0.05	0.25	0.22	0.04–0.90	0.33	0.22	0.05–1.50	0	0.25
11H-Benzo[a]fluoren-11-one	11H-BAF	0.02	0.91	0.68	0.10–3.70	1.43	0.94	0.20–8.60	0	0.06
Bezo[c]fluoren-11-one	BCF11	0.02	0.08	0.06	0.02–0.40	0.12	0.09	0.03–0.60	1	0.06
Benzo[b]fluoren-11-one	BBF11	0.02	0.21	0.15	0.02–0.90	0.35	0.24	0.06–1.80	1	**0.03**
7H-Benz[de]anthracen-7-one	7H-BDEA	0.05	0.43	0.29	0.06–2.00	0.61	0.50	0.10–2.60	1	0.08
Benz[a]anthracene-7,12-dione	BAA7,12	0.05	0.06	0.05	0.01–0.20	0.11	0.07	0.02–0.50	5	**0.01**
n-Alkanes										
Octadecane	C18	0.05	0.55	0.49	0.10–1.40	0.73	0.57	0.06–2.30	0	**0.03**
Nonadecane	C19	0.05	0.55	0.47	0.10–1.50	0.82	0.65	0.20–2.60	0	**0.03**
Eicosane	C20	0.05	1.08	1.00	0.20–4.00	1.14	0.89	0.20–4.00	0	0.23
Heneicosane	C21	0.05	1.77	1.48	0.40–10.10	1.79	1.48	0.20–5.90	0	0.10
Docosane	C22	0.05	2.97	2.24	0.40–18.90	2.64	2.24	0.30–8.00	0	0.08
Tricosane	C23	0.05	4.02	2.60	0.50–21.70	3.05	2.72	0.60–9.20	0	0.17
Tetracosane	C24	0.05	3.76	2.60	0.60–14.70	2.92	2.47	0.60–8.60	0	0.16
Pentacosane	C25	0.05	2.87	1.81	0.50–15.10	2.28	1.89	0.60–6.80	0	0.25
Hexacosane	C26	0.05	2.43	1.61	0.40–12.20	1.79	1.50	0.40–5.00	0	0.24
Heptacosane	C27	0.05	3.80	2.49	0.90–15.70	2.40	1.75	0.70–7.70	0	0.95
Octacosane	C28	0.05	2.43	1.74	0.60–8.70	1.64	1.43	0.50–4.00	0	0.46
Nonacosane	C29	0.05	4.64	3.48	1.10–13.60	2.41	2.04	0.70–7.20	0	0.19
Triacontane	C30	0.05	2.44	1.64	0.30–13.60	1.11	0.90	0.30–3.10	0	0.36
Hentriacontane	C31	0.05	4.92	3.65	1.10–18.20	2.62	1.77	0.90–8.10	0	0.08
Dotriacontane	C32	0.05	1.56	1.09	0.20–7.50	0.69	0.53	0.20–1.90	0	0.78
Tritriacontane	C33	0.05	1.93	1.30	0.40–6.20	1.03	0.59	0.30–3.00	0	0.52
Tetratriacontane	C34	0.05	0.39	0.31	0.08–1.20	0.17	0.15	0.04–0.60	0	0.41
Pentatriacontane	C35	0.05	0.31	0.26	0.06–0.90	0.16	0.13	0.04–0.60	1	0.30
Hexatriacontane	C36	0.05	0.21	0.18	0.05–0.60	0.11	0.11	0.03–0.40	11	0.21
Iso & anteiso-alkanes										
Iso-Nonacosane	i-C29	0.05	0.64	0.41	0.05–2.90	0.19	0.14	0.03–0.70	0	**0.01**
Anteiso-Nonacosane	a-C29	0.05	0.19	0.14	0.01–0.60	0.15	0.09	0.04–0.50	0	0.84
Iso-Triacontane	i-C30	0.05	0.23	0.13	0.02–1.40	0.17	0.07	0.03–1.40	0	0.70
Anteiso-Triacontane	a-C30	0.05	0.75	0.50	0.04–2.80	0.54	0.31	0.10–1.70	0	0.30
Iso-Hentriacontane	i-C31	0.05	1.40	1.04	0.30–5.40	0.77	0.44	0.20–2.30	1	**0.05**
Anteiso-Hentriacontane	a-C31	0.05	0.19	0.14	0.02–0.80	0.14	0.08	0.04–0.40	1	0.53
Iso-Dotriacontane	i-C32	0.05	0.28	0.24	0.03–1.00	0.19	0.11	0.03–0.60	1	0.93
Anteiso-Dotriacontane	a-C32	0.05	1.33	0.89	0.20–5.00	0.81	0.43	0.20–2.70	1	0.08
Iso-Tritriacontane	i-C33	0.05	0.82	0.59	0.10–2.80	0.42	0.23	0.05–1.60	1	0.06
Anteiso-Tritriacontane	a-C33	0.05	0.17	0.09	0.02–2.00	0.07	0.04	0.01–0.20	3	0.24
Hopanes										
18α(H)-22,29,30-Trisnorhopane	Ts	0.05	0.86	0.71	0.10–2.20	0.53	0.46	0.20–2.10	12	**0.01**
17α(H)-22,29,30-Trisnorhopane	Tm	0.05	0.92	0.68	0.20–4.50	1.13	0.57	0.20–5.30	15	0.50
17β(H)-22,29,30-Trisnorhopane	27b	0.05	0.21	0.19	0.03–0.60	0.52	0.33	0.10–2.50	45	0.09
17 α(H)21β(H)-30-Norhopane	29ab	0.05	2.86	1.94	0.60–10.00	2.19	1.29	0.30–12.70	3	0.28
17β(H)21α(H)-30-Norhopane	29ba	0.05	0.46	0.34	0.10–1.80	0.58	0.46	0.10–3.60	24	0.46
17α(H)21β(H)-Hopane	30ab	0.05	2.49	1.78	0.70–8.40	1.93	0.97	0.20–11.00	3	0.30
17β(H)21α(H)-Hopane (Moretan)	30ba	0.05	0.42	0.38	0.10–1.20	0.53	0.35	0.10–3.50	31	0.53
22S-17α(H),21β(H)-Homohopane	31abS	0.05	1.05	0.65	0.10–4.70	0.77	0.41	0.20–5.00	4	0.20
22R17α(H),21β(H)-Homohopane	31abR	0.05	1.36	1.02	0.20–5.90	1.21	0.97	0.20–4.80	4	0.58
22S-17α(H),21β(H)-Bishomohopane	32abS	0.05	0.69	0.53	0.10–2.40	0.67	0.39	0.10–2.70	35	0.94
22R-17α(H),21β(H)-Bishomohopane	32abR	0.05	0.53	0.39	0.10–2.90	0.52	0.47	0.20–1.60	35	0.99
Cholesterol										
Cholesterol	CHO	0.05	1.11	0.56	0.10–18.70	0.86	0.52	0.10–5.50	19	0.60
Fatty acids										
Palmitic acid	PAL	0.10	255	231	167–666	414	363	182–2324	15	**0.01**
Linoleic acid	LINA	0.01	0.15	0.05	0.01–1.50	0.48	0.15	0.04–5.60	12	0.19

(*continued on next page*)

Table 1 (*continued*)

Substance	Abbreviation	Before LEZ (2006–2007), $n = 40$				After LEZ (2009–2010), $n = 35$			% < LOQ	*t*-Test (*P* value)
		LOQ	Mean	Median	Range	Mean	Median	Range		
Oleic acid	OLA	0.05	3.96	1.28	0.30–42	7.62	3.44	0.30–55.80	1	0.16
Stearic acid	STA	0.10	39.20	36.47	25–67	65.10	51.20	21–456	0	**0.04**
Resin acids										
Isopimaric acid	ISPA	0.02	4.13	2.17	0.30–31.20	3.05	2.54	0.40–8.80	9	0.27
Dehydroabietic acid methylester	DHAA-me	0.02	7.51	6.17	2.40–23	10.15	7.00	4.40–48	3	0.09
Dehydroabietic acid	DHAA	0.10	146	106	21–682	157	136	28–574	6	0.77
Anhydrous sugars										
Galactosan	GAL	0.10	6.20	3.00	0.30–30.20	5.27	3.57	1.472–21.85	8	0.78
Mannosan	MAN	0.10	31.20	17.30	2–130	16.00	12.50	1.2–51	0	**0.01**
Levoglucosan	LEVO	0.10	155	145	40–575	201	182	84–381	0	**0.05**
Phenolic compounds										
Vanillin	VAN	0.05	1.20	0.75	0.20–11.00	0.60	0.40	0.20–3.30	8	0.35
Vanillic acid	VANA	0.05	0.18	0.06	<LOQ –1.50	0.05	0.03	<LOQ –0.20	4	**0.04**
Acetosyringone	ASYG	0.01	0.07	0.04	<LOQ –0.30	0.02	0.01	<LOQ –0.10	4	**0.01**
Syringylacetone	SYGA	0.01	0.03	0.01	<LOQ –0.40	0.01	0.01	<LOQ –0.03	7	**0.04**
Syringic acid	SYRA	0.01	0.04	0.02	<LOQ –0.40	0.01	0.01	<LOQ –0.04	1	**0.03**
Carbon fraction										
Elemental carbon	EC	0.04	2.50	2.00	0.80–6.50	2.20	2.10	1.00–3.90	0	**0.04**
Organic carbon	OC	0.16	2.50	1.90	0.60–7.40	1.80	1.70	0.20–4.20	0	0.90

Bold values represents *P*-values less than 0.05.

expected emission sources in Lothstrasse sampling site due to its location in the inner city of Munich near to a main road. The 3 and 4 factors solution were rejected because they were not able to separate the traffic source from the other emission source from mixed sources.

Therefore, 5-factors solution was performed and gave a good separation of traffic source from the other sources. The 6-factors solution was also rejected because of the splitting of the factors with no reasonable interpretation. The 5-factors solution had afforded the most reasonable interpretation of the source profiles, which were related to primary PM emissions.

3.2.2. Sources from POC data

The main possible sources of POC have been identified using the data of 75 samples from the both sampling periods with 67 POC for each sample as inputs for EPA-PMF 3.0. A five-factor solution was resolved by PMF and each of these five factors was dominated by the pattern of species that can be associated with a specific source or with groups of sources. The separated factors represent emissions from traffic, solid fuels combustion (most likely combustions from wood and brown coal), cooking and mixed sources. The PMF factor profiles and their contributions for the five-factor solution are presented in Figs. 4 and 5 respectively.

More than 70% of hopanes from mineral-oil-derived emission sources were attributed to the first factor. The homohopane index (31abs/31abs + 31abR) (Schnelle-Kreis et al., 2007) value was found to be 0.46. Hopanes are unique source markers for fossil fuel combustion. Due to their unique chromatographic distribution, hopanes can be easily identified by GC/MS with m/z 191 as the characteristic ion. It has been confirmed that hopanes found in automobile exhausts are not from gasoline and diesel fuel, but from lubricating oil based on the similarity of the hopanes distributions (Li, 2003). About 45% of EC, which is associated commonly with motor vehicle emissions (Baccarelli et al., 2011; Shrivastava et al., 2007) was associated also with this factor. Hopanes and EC are important markers for motor vehicle emissions (Shrivastava et al., 2007). In addition high percentage, about 45% of the n-alkanes with carbon preference index (CPI) of 1.4 were also associated with this factor. CPI values for n-alkanes in vehicular emissions are close to unit (CPI ≈ 1) (Kavouras et al., 1999). Therefore, factor 1 was considered as traffic emissions.

Factor 2 was characterized by more than 40% of each of levoglucosan and dehydroabietic acid. Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a pyrolysis product from cellulose. It has been proposed as one marker of wood smoke because of its stable properties in the atmosphere (Heringa et al., 2011). Furthermore, levoglucosan is exclusively in the fine particle phase and constitutes a large fraction of the emitted particles, making it a suitable marker of fine particulate matter ($PM_{2.5}$) originated from biomass burning (Hedberg et al., 2006). Relative kinetics indicates that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when wood combustion particles are exposed to 1×10^6 molecules cm^{-3} of OH (typical average summertime conditions). This implies that levoglucosan reacts with OH on a timescale similar to that of transport and deposition, which has important implications for the use of levoglucosan as a tracer for biomass burning emissions in source apportionment studies (Hennigan et al., 2010). Dehydroabietic acid has been suggested as a marker for wood smoke. Unlike levoglucosan, which can be used to trace all wood combustion, dehydroabietic acid is found solely in emissions from burning of coniferous wood and therefore can be used to distinguish coniferous wood from hardwood combustion (Leithead et al., 2006). High percentage of retene, about 40% and 20–65% of the O-PAH, were also associated with this factor. Factor 2 therefore was considered as a first solid fuel combustion with some wood combustion influence.

However, the levoglucosan to OC ratios have been used to evaluate the contribution of biomass burning to the aerosol OC showing that the higher contribution of levoglucosan to OC in ambient air indicates the influence of wood combustion (Zdráhal et al., 2001). The levoglucosan to OC ratio in this study is only 0.07, which is relatively low. This may be the reason for low contribution of organic compounds originating from wood combustion to that factor here (i.e. this solid fuel factor is not much dominated by PAH, unlike in other places with high wood combustion influence (Schnelle-Kreis et al., 2007)). In addition, other investigations have shown big differences in levoglucosan to OC ratios depending on the wood and wood combustion appliance type. Solid fuel combustion using coal emits a large amount of carbonaceous aerosol containing organic constituents such as PAH and O-PAH (Lighty et al., 2000). As the second solid fuel combustion factor (factor 3) is dominated by a high concentration of picene – which is considered to be a marker of coal combustion (Bi et al., 2008; von Schneidemesser et al., 2010), its likely influenced by this source. Also the homohopane index for hopanes pattern was found to be 0.15 which is similar to emissions from brown coal combustion (Bi

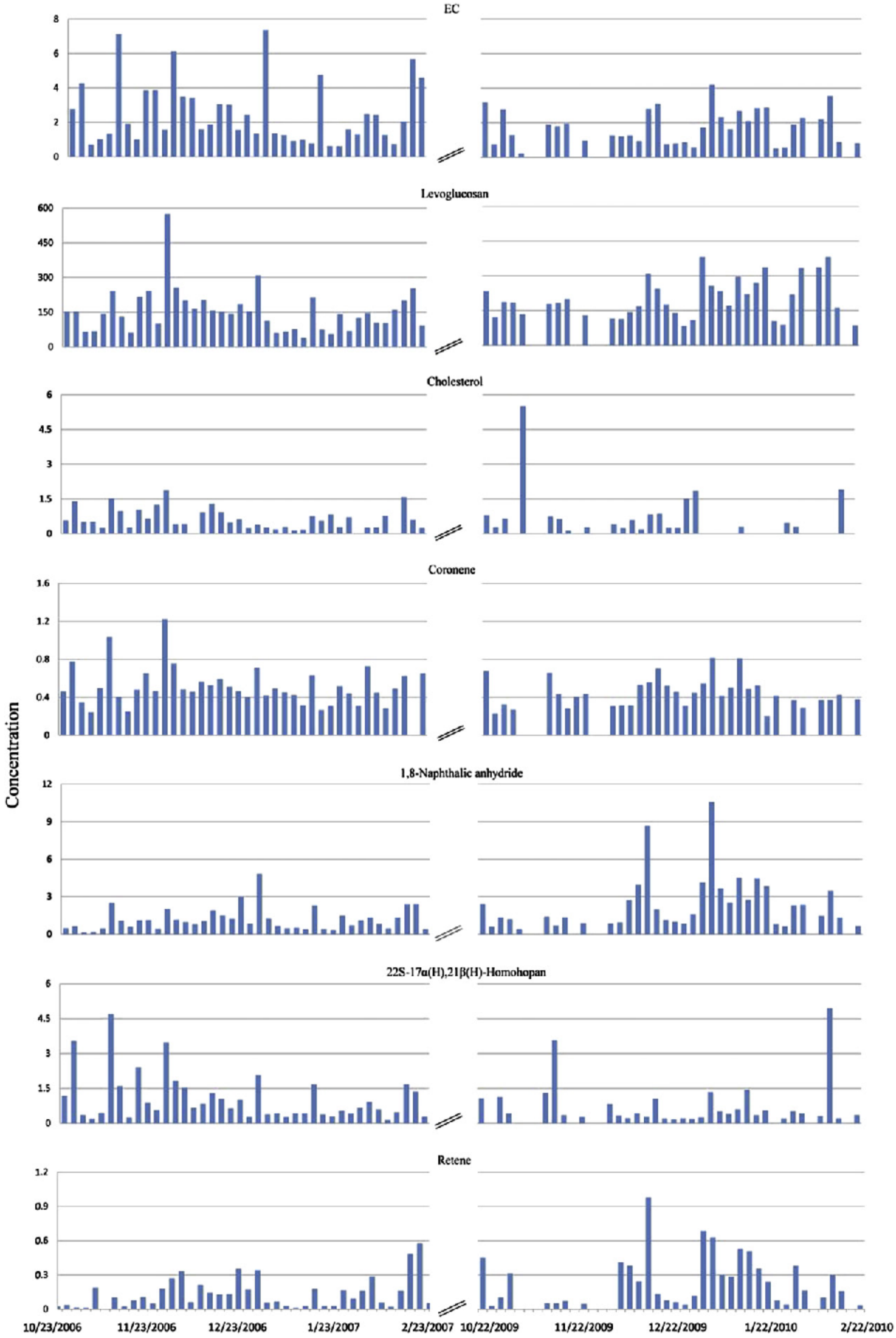

Fig. 3. Time series of EC (µg m^{-3}) and some selected POC (ng m^{-3}).

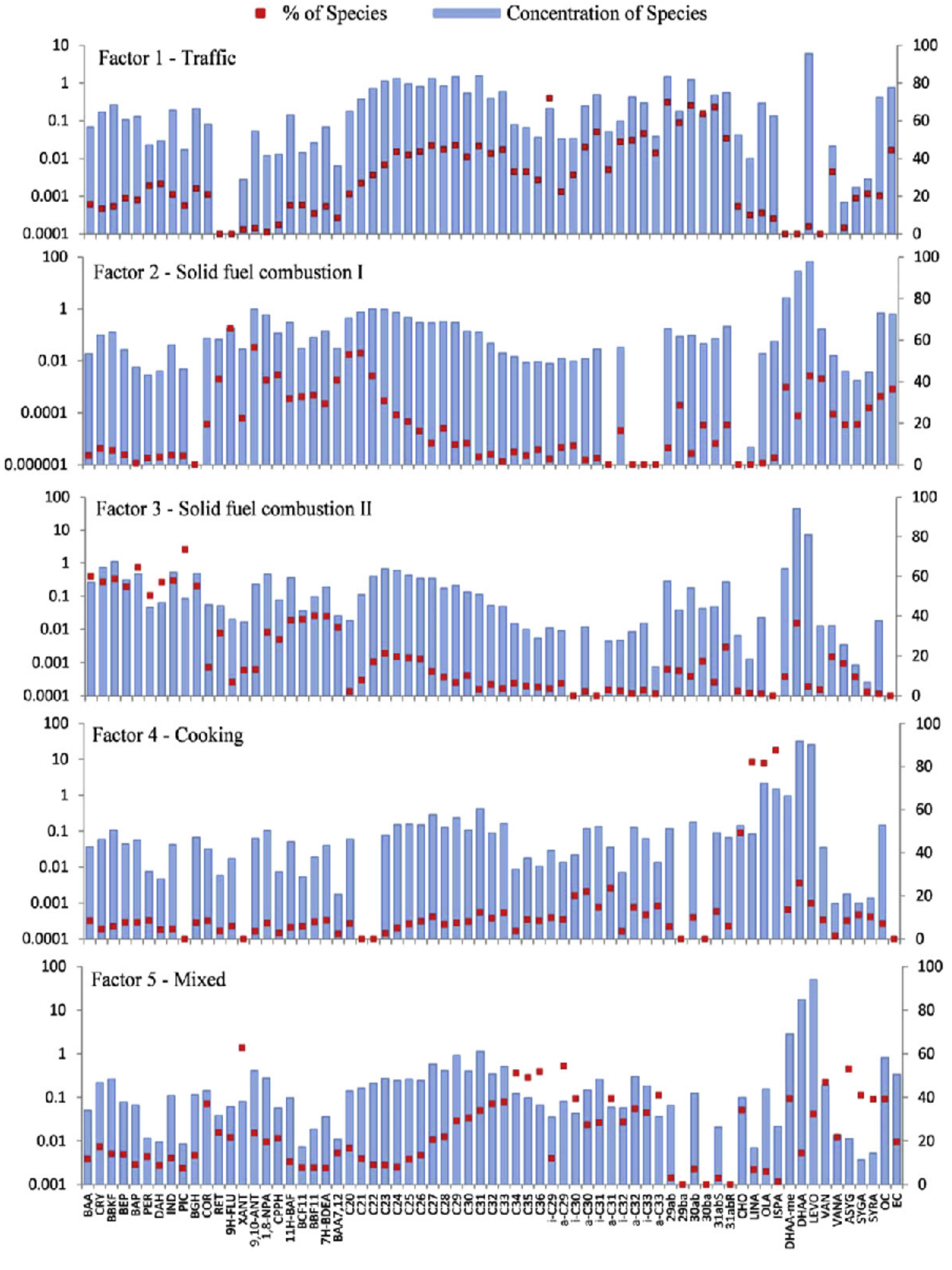

Fig. 4. PMF factor profiles.

et al., 2008). The homohopane index found in emissions from coal combustion ranged from about 0.1 for lignite coal to about 0.4 for bituminous coal (Schnelle-Kreis et al., 2007). The use of lignite briquettes (brown coal) is common for keeping fire going on overnight in the wood burning stoves during winter. Factor 3, the second solid fuel combustion factor, thus is considered as influenced by brown coal combustion. In this context it has to be considered that local emissions often have an impact, particularly under unfavorable dispersion conditions (weak wind conditions, inversion weather conditions) (Brandt et al., 2011). Local influence may explain the somewhat unexpectedly high contribution of PAH to the second solid fuel factor.

Factor 4 was characterized by about 50% of cholesterol, which is also an important marker for meat cooking emissions (Robinson et al., 2006). More than 80% of the fatty acids were also associated with this factor. Organic molecular such as oleic acid, palmitoleic acid, and cholesterol are the markers of cooking emissions (Shrivastava et al., 2007). Food cooking has been shown to be an important source of the fine organic aerosol in urban environments (Robinson et al., 2006). This factor was considered as cooking emissions.

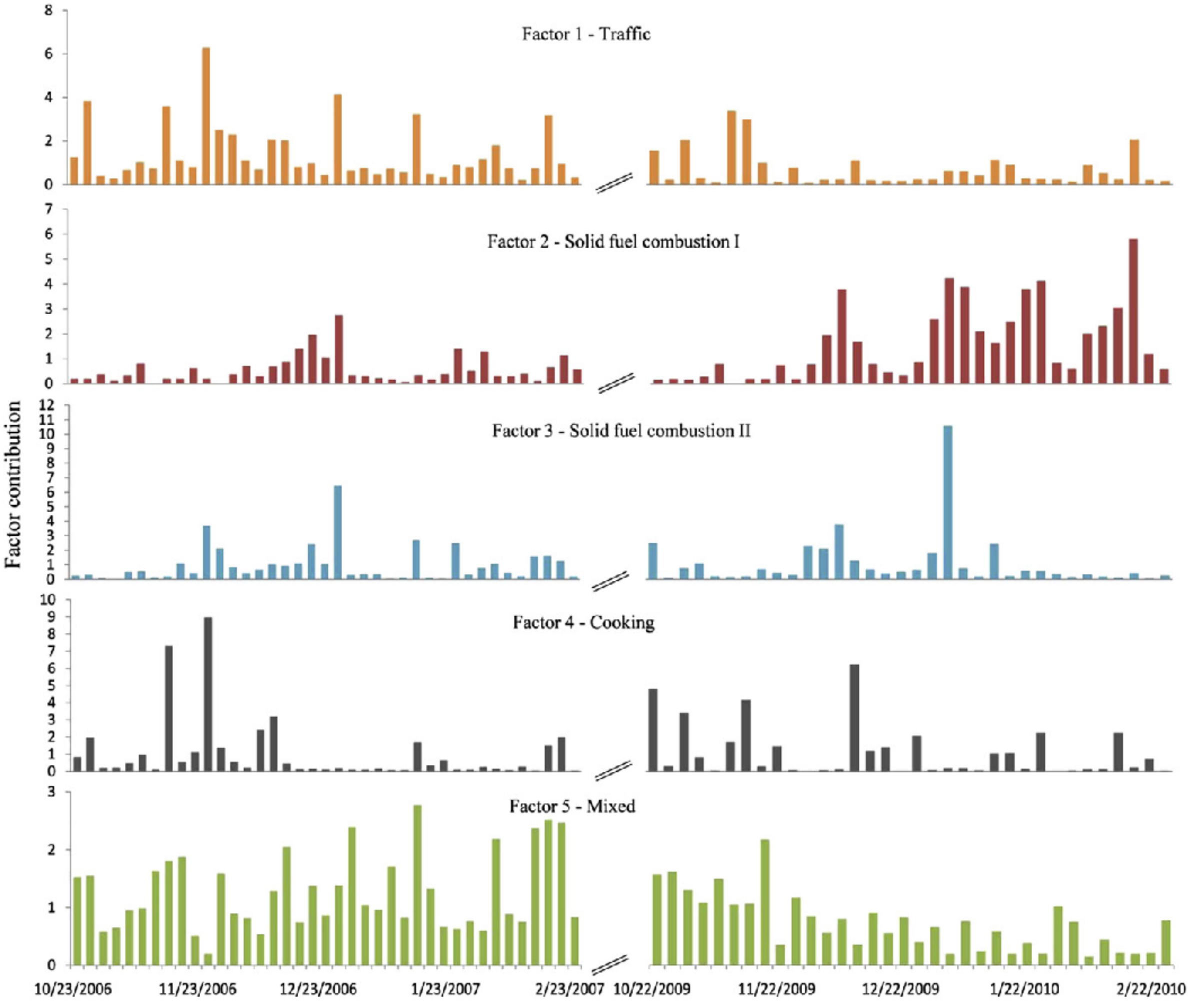

Fig. 5. PMF factors contribution.

The last factor could not be attributed to a single source class and therefore was considered as mixed sources factor. It was characterized by compound patterns which represents a mixture sources from tobacco smoke because of specific pattern of iso & anteiso alkanes (Rogge et al., 1994) and n-alkanes with CPI ≈ 2 (Finlayson-Pitts et al., 2000). Emissions from cooking (e.g., cholesterol) and wood combustion (e.g., levoglucosan and dehydroabietic acid) were also associated. This factor was dominated also by high concentrations of acetosyringone, syringylacetone and syringic acid which are the molecular markers for hardwood smoke (Nolte et al., 2001; Shrivastava et al., 2007). Vanillin and vanillic acid were also associated with this factor. Syringyl compounds derived from sinapyl alcohol are generally more abundant in the hardwood smokes than their guaiacyl analogs derived from coniferyl alcohol, though lesser amounts of these are also present (Nolte et al., 2001).

3.2.3. Factors contribution and LEZ implementation

Fig. 5 shows the differences between the contributions of source factors for the two sampling periods. The contribution of traffic factor was decreased about 60% after the implementation of the LEZ. The average concentration of EC from traffic factor decreased from 1.1 μg/m^3 before the implementation of the LEZ to 0.5 μg/m^3 after the implementation of the LEZ. Diesel exhaust particles are a significant contribution to the local urban PM$_{2.5}$ levels and are a dominant source of atmospheric EC (Schauer, 2003). Also it is worth to mentioning the legally supported car scrappage scheme (the so called “Abwrackprämie” in Germany) which may be also involved in the observed reduction of EC levels. In the beginning of the year 2009, during the global financial crisis, the German federal government subsided the exchange of old cars by new ones in order to support car makers. This process leads to a more environment friendly car fleet across the country as the EC emission rates of new vehicles are much lower than those of the older ones (Sonntag et al., 2012). The pre-stage of LEZ implementation in Munich city also enhanced the effect of LEZ by preventing the heavy duty vehicles permanently from going through LEZ areas.

The contribution of the first solid fuel combustion factor with wood combustion influence was increased about 180% in the second sampling period due to the colder winter of 2009/10. The average concentration of levoglucosan, dehydroabietic acid, 1,8-naphthalic anhydride and retene in this factor increased from 47.40, 20.40, 0.40, 0.07 ng/m^3 before the implementation of the LEZ to 85.27, 36.80, 0.74, 0.13 ng/m^3 after the implementation of the LEZ respectively. Depending on the information from the Federal Ministry for Food, Agriculture and Consumer Protection (Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz, BMELV in German), the prices of heating oil in Germany raised up from 55 to 92 Cent/l because of the global financial crisis (which happened in 2008). On the other hand, the prices of wood pellets were stable around 200 Euro/t (BMELV, 2011). This may lead to the use of wood pellets instead of heating oil across Germany for domestic heating purposes.

The contribution of second solid fuel combustion factor, which is most likely brown coal combustion, increased about 10% in the second sampling period. That was correlated with increasing of the wood combustion contribution. The contribution of the cooking factor showed no noticeable difference between the two sampling periods. The contribution of the mixed sources factor was decreased in the range of 40% in the second sampling period 2009/10. The metrological data (which provided by BLfU) showed that the wind direction (WD) and speed (WS) were very similar in both sampling periods. In consequence, there were no detectable effects of WD and WS neither on POC concentrations nor on the contribution of the source factors.

4. Conclusion

A study of chemical compositions and sources of ambient particles in Munich has been carried out over two different periods, before (2006–2007) and after (2009–2010) the implementation of LEZ. The concentrations of POC measured from the two sampling periods were compared, allowing for a thorough monitoring of the LEZ implementation effect upon the reduction of hazardous, particle associated organic substances and the different sources of PM pollution. In general, there has been a positive effect of implementation of LEZ on the reduction of POC concentrations but not significantly because of the variation of sources of POC. PMF model has been applied to chemical composition data to identify the main sources of POC. Five factors have been separated using POC data. Traffic, first solid fuel (wood) combustion, second solid fuel (brown coal) combustion, cooking and mixed sources were the main contributors to $PM_{2.5}$ in Lothstrasse sampling site in Munich. These results are expected for the location of the sampling site which is a traffic influenced station with approximately 41 000 passing vehicles per day and the local area is mainly composed of habitation, trade and commerce (BSUGV, 2004). Different contributions have been noticed for all five factors between the two sampling periods. The contribution of traffic and mixed sources factors decreased about 60% and 40% respectively after the implementation of the LEZ. The average concentration of EC in the traffic factor decreased from 1.1 μg/m^3 to 0.5 μg/m^3 giving a positive effect for the reduction of vehicular emissions because exposures to traffic-related EC is related to decrements in lung function (Barraza-Villarreal et al., 2011). The contribution of the first solid fuel (wood) combustion factor has increased in the second sampling period about 180% due to the colder winter in 2009/10 comparing with winter in 2006/07. The average concentration of levoglucosan, dehydroabietic acid, 1,8-naphthalic anhydride and retene in the first solid fuel combustion factor increased from 47.40, 20.40, 0.40, 0.07 ng/m^3 before the implementation of the LEZ to 85.27, 36.80, 0.74, 0.13 ng/m^3 after the implementation of the LEZ respectively. More investigations in the domain of health effects of solid fuel combustion like wood and coal combustion will be conducted by Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – HICE (http://www.hice-vi.eu).

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PUBLICATION 3

Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach

by

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The laboratory analysis of organic compounds was performed by Raeed Megeed Qadir and other CMA group members. Raeed Megeed Qadir was responsible for proceeding and preparing data sets for the positive matrix factorization (PMF) analysis and wrote the part of the paper which related to applying PMF model, results, interpretation and the discussion of PMF results. The final evaluation and interpretation of the results were performed in close cooperation with the co-authors.

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Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach

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Abstract

Children are particularly susceptible to air pollution and schools are examples of urban microenvironments that can account for a large portion of children's exposure to airborne particles. Thus this paper aimed to determine the sources of primary airborne particles that children are exposed to at school by analyzing selected organic molecular markers at 11 urban schools in Brisbane, Australia. Positive matrix factorization analysis identified four sources at the schools: vehicle emissions, biomass burning, meat cooking and plant wax emissions accounting for 45%, 29%, 16% and 7%, of the organic carbon respectively. Biomass burning peaked in winter due to prescribed burning of bushland around Brisbane. Overall, the results indicated that both local (traffic) and regional (biomass burning) sources of primary organic aerosols influence the levels of ambient particles that children are exposed at the schools. These results have implications for potential control strategies for mitigating exposure at schools.

Capsule abstract:

The identification of the most important sources of primary organic aerosols at urban schools has implications for control strategies for mitigating children's exposure at schools.

Keywords

Positive Matrix Factorization, Sources, Primary organic aerosols, Exposure, Schools

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1.0 Introduction

Organic aerosols are frequently the largest component of ambient fine particles in urban atmospheres (Jimenez et al., 2009). These aerosols are a complex mixture of around 10^5 and 10^6 compounds (Goldstein and Galbally, 2007) from a number of primary and secondary sources, where sources that directly emit particles into the atmosphere can be referred to as primary sources. Whereas secondary sources refer to particles formed by reactions in the atmosphere of gaseous species in the atmosphere, such as the photo-oxidation of volatile organic compounds (Seinfeld and Pandis, 2006). In an urban environment primary sources of particles can include vehicle emissions, biomass burning (from both domestic and natural sources), coal combustion, cooking, plant abrasion and paved road dust (see e.g. (Qadir et al., 2013; Schnelle-Kreis et al., 2007; Shrivastava et al., 2007)). For these primary sources there are a number of organic markers that are known to be characteristic of a specific emission source and crucially also have a long lifetime in the atmosphere to enable detection at monitoring stations (Cass, 1998). Examples of some of the more specific organic markers include levoglucosan for biomass burning (Robinson et al., 2006a) and cholesterol for meat cooking (Kleeman et al., 2008). Hopanes are present in fossil fuels, and the different hopanoid compounds are specific to the different types of fossil fuels such as coal, petroleum and lubricating oil ((Schnelle-Kreis et al., 2005) and references therein)). Thus these organic compounds along with others can be used as molecular markers for identifying the contributing sources of primary organics to ambient particles.

A quantitative assessment of the contribution of emission sources is available using positive matrix factorization (PMF), which has been successfully applied previously to organic molecular datasets (Qadir et al., 2013; Schnelle-Kreis et al., 2007; Shrivastava et al., 2007). Assessing the contribution of primary sources is important as there are numerous detrimental health effects associated with exposure to airborne particles (Heal et al., 2012; Rückerl et al., 2011). In particular, children have been shown to be more susceptible to the health effects associated with exposure to airborne particles (Rückerl et al., 2011), and several studies have linked exposure to vehicle emissions to increased risks of developing asthma and wheezing (Gehring et al., 2010; Ryan et al., 2009). Children spend a large portion of their day at school. Consequently schools represent a location accounting for a significant fraction of their overall daily exposure. Schools are also unique urban environments that are influenced not only by local and regional sources but also by school-related activities such as drop-off/pick-up traffic, which may result in increased exposure to vehicle emissions. However, there is limited information on children’s exposure to vehicle emissions and other sources in the literature (Mejía et al., 2011).

Considering the aforementioned gaps in knowledge, the present study aimed to determine the primary sources of the ambient fine particulate matter present at urban schools by quantifying the levels of selected organic molecular markers. PMF, a receptor model (Paatero and Tapper, 1994), was applied in order to quantitatively determine the contributions of these sources to levels of ambient particles at the schools. This enabled the driving factors to the levels of different primary sources to be investigated and we hypothesized that vehicle emissions will be the main primary source contributing to children’s exposure at school due to the schools’ selection criteria, outlined in the next section.

2.0 Method

2.1 Sampling sites

The 11 schools selected for this study, which will be referred to as S15 to S25, are in different suburbs in the city of Brisbane, Australia. “The school locations are depicted in Figure S1, Supporting Information, while schematic maps of the schools and surrounding roads can be found in Salimi et al. (2013).” This chemical sampling was a part of a larger campaign to study the effect of ultrafine particle from traffic emissions on children’s health, known as UPTECH (www.ilaqh.qut.edu.au/Misc/UPTECH%20Home.htm). In this study 25 schools participated but only at the last 11 schools were filters collected for this analysis due to instrument availability. The sampling campaign for the current paper was conducted from November 2011 till August 2012.

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The schools that were chosen were not near any other large source of air pollution, other than road traffic and were also not close to any large infrastructure projects. A site close to the middle of the school which gave the best overall representation was chosen to conduct the measurements and sampling at each school. Inlets for the sampling were placed on the top of a trailer, which served to house all of the instruments at the site including an automatic weather station (Monitor Sensors). Data from nearby weather stations was also obtained from the Bureau of Meteorology (BOM) and Queensland Department of Science, Information Technology, Innovation and the Arts (DSITIA) as some of the schools would have been affected by local winds due to schools buildings. Sampling inlets were approximately 3m off the ground. Traffic counts were taken on the busiest road next to the school, referred to as the main road throughout. In the traffic count, vehicles that were classified as light were cars, motorbikes and scooters. Trucks with 2, 3 and 4 axels were classified as medium vehicle and long articulated trucks classified as heavy vehicles.

2.2 Sampling methodology

The particle size fraction was selected using a low-volume $PM_{2.5}$ cyclone and the required flow rate for the cyclone was maintained using critical orifices. The particles were collected in polycarbonate filter holders on 47 mm, Quartz fiber filters (Whatman) which was pre-treated at 500°C for 1 hour prior to use. The sampling period was from 08:00 until 08:00 the next day, Monday to Friday for one week to give a total of four samples at each school. This sampling regime typically gave sampling volumes of 6 m^3. After sampling each filter was placed in a Petri dish and covered in aluminum foil. The samples were then sealed in a ziplock bag and frozen until analysis. The flow rate for the cyclones was checked at the beginning of each sample and always set to within ±0.1 liters per minute of the desired flow rate. Field blanks were collected at each school and all results were field-blank corrected.

2.3 Chemical analysis

The organic composition of the samples was analyzed using In-situ Derivatization Thermal Desorption (IDTD) followed by Gas Chromatography Time-Of-Flight Mass Spectrometry (GC-TOF-MS) (Orasche et al., 2011; Schnelle-Kreis et al., 2011) at the Joint Mass Spectrometry Centre, Helmholtz Zentrum München, Neuherberg, Germany. In brief, filter punches were placed in an injection liner and spiked with internal standards (isotope labeled reference compounds) and 10 µl derivatizing agent N-Methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA). An automated sampling robot exchanged the complete GC liners placed in the injector which is automatically closed and opened by a liner exchanging unit (Linex, Atas GL, Netherlands). During thermal desorption (16 min, 300 °C) MSTFA enriched carrier gas was passed through the liner. Desorbed and derivatized molecules were focused at 70 °C on the head of a nearly non-polar capillary column, BPX5, 25 m, 0.22 mm ID, 0.25 µm film (SGE, Australia) which was installed in an Agilent 6890 gas chromatograph (Agilent, USA). After the isothermal run at 70 °C, the temperature was increased to 130 °C within one minute. Then the rate was lowered to 8 °C min^{-1} until a temperature of 330 °C was reached followed by an isothermal time of 30 min. The detection of compounds was carried out on a Pegasus III TOFMS (LECO, USA). The data acquisition frequency was 25 spectra per second within a mass-to-charge range of 35 to 500. The detection limits for the targeted compounds can be found in Tables S1 and S2 (Supporting Information).

Details of the elemental carbon (EC) and organic carbon (OC) analysis can be found in Crilley et al. (2013). Briefly, $PM_{2.5}$ samples were collected concurrently at the same location at each school and were analysed according to the IMPROVE method on a thermal/optical transmittance carbon analyser (Sunset Laboratories) (Chow et al., 2001).

2.4 Data analysis

Positive Matrix Factorization (PMF) was performed in this study using the EPA PMF v3.0, developed by the U.S EPA (US-EPA, 2008). A total of 21 organic compounds were used in the initial analysis and these included n-alkanes from $C_{20\text{-}33}$, four hopanes, cholesterol, dehydroabietic acid and its methylester, levoglucosan, mannosan, EC and the OC fraction. Missing values in a certain school site were replaced with the geometric mean at the same site and the uncertainty was set to four times the geometric mean for those values. Species with more than 50% of data below the limit of quantification (LOQ) were excluded from the inputs. Therefore, some alkanes (C_{20}, C_{21}, C_{26}, C_{28}, C_{32} and C_{33}), dehydroabietic acid and its methylester, and mannosan were excluded from the PMF analyses. In other few cases the values were replaced with half of the LOQ and the uncertainties set to 5/6 of the LOQ. For the other data, the uncertainties are set according to the following equation:

$$u = [(\text{error fraction} \times \text{concentration})^2 + (\text{LOQ})^2]^{0.5} \qquad (1)$$

where error fraction is the percentage of uncertainty, LOQ is the limit of quantification. Overall error fractions were estimated from sampling and analytical errors. Species with low signal to noise ratio ($S/R<2$), were assigned as weak. One hundred bootstrap runs were performed to assess the uncertainty of the factor loadings and profiles. Changing the Fpeak value did not improve the source profiles or Q value and so base model results (Fpeak=0) are reported. The PMF solutions are discussed in Section 3.3.

The other data analysis technique employed was one way ANOVA used to compare the concentrations between the seasons and this was performed using SPSS v19.

3.0 Results and discussion

3.1 General school characteristics

The sampling was conducted over almost a full year and covered both winter and summer, as reflected in the meteorological conditions described in Table 1. Brisbane is a subtropical city with the mean temperatures ranging from 14 to 25°C (Table 1). October till April is warmer with higher humidity and this period is referred to as summer. May till September is cooler with typically more stable weather and it is referred to as the winter months. A range of traffic conditions were also observed at the schools (Table 2). Some of the schools were on busy arterial roads (S19, S20) while others were in residential areas with low traffic counts (S16, S18, S21). There were also schools alongside roads that service commercial/light industrial areas (S23, S25) and such schools recorded a higher proportion of heavy and medium vehicles (Table 2). Based on the organic compounds detected and their relative abundance, the major contributing sources of primary organic aerosols were determined at the schools and discussed in the next sections.

Table 1: Average meteorological conditions of the schools studied during the sampling week.Note that temperature and relative humidity reading were taken from the school weather station while wind speed measurements were from the closest BOM or DSTIA stations.

	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25
Sampling Date	Nov 2011	Nov 2011	Dec 2012	Mar 2012	Mar 2012	Apr 2012	Jun 2012	Jun 2012	Jul 2012	Aug 2012	Aug 2012
Temperature (°C)	24	25	24	22	23	20	14	14	15	15	15
Relative Humidity (%)	65	75	71	71	79	63	58	66	60	40	68
Wind Speed $(m\ s^{-1})$	4.1	1.0	0.91	1.0	3.3	0.7	0.8	0.6	0.7	3.0	3.5

Table 2: Mean traffic conditions from the main at the schools studied over the sampling week

	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25
Traffic $(Veh\ hr^{-1})$	858	46	757	35	1093	1121	151	469	657	160	332
Light vehicles (%)	92.1	97.8	95.3	97.9	89.9	96.2	97.4	96.8	71.1	97.1	92.0
Medium vehicles (%)	5.9	1.6	3.0	2.1	3.2	2.5	2.1	2.5	28.0	2.4	6.5
Heavy vehicles (%)	0.9	0.4	0.6	0.0	2.0	0.8	0.4	0.6	0.6	0.5	1.2

3.2 Detected organic compounds at the schools

A number of particulate organic compounds were detected at the schools as summarized in Table 3, which demonstrates that the organic species and their concentrations varied from school to school. Of the analysed species, the most abundant organic compound was generally levoglucosan, which was detected at all of the schools except for S16 (Table 3). Of the other anhydrous sugars targeted, mannosan and galactosan were detected only at school sampled in summer at S21-5 and S22, S24-5, respectively (Table 3). The most abundant resin acids detected were dehydroabietic acid (DHAA) and dehydroabietic acid methyl ester (DHAA-ME), and these compounds were observed only at the schools sampled in summer (Table 3). Cholesterol, a known tracer molecule for meat cooking emissions, was observed at the schools (Table 3) (Kleeman et al., 2008), indicates that cooking was a source. The most abundant hopanes were 17α(H),21β(H)-30-norhopane (29ab) and 17α(H),21β(H)-hopane (30ab) at all of the schools. In addition, 17α(H),21β(H)-22S-homohopane (31abS) and 17α(H),21β(H)-22R-homohopane (31abR) were detected at S18-25 in appreciable quantities. The n-alkanes analyzed were octadecane (C_{18}) to hexatriacontane (C_{36}) and their concentrations and distributions varied across the schools. The average values for each alkane at the schools are given in Table S2. Throughout this paper, the n-alkanes are referred to as C_n, where n indicates the number of carbon atoms. For example, pentacosane is referred to as C_{25}. All abbreviations are listed in Table S2. The range of n-alkanes detected at the schools indicated that fossil fuel combustion was another significant source at the schools, which is investigated further in the next section.

Table 3: Average concentrations (in ng m^{-3}) of selected hopanes and polar organic compounds along with calculated values for the alkanes at each school with avearge of EC and OC (in µg m^{-3}). Abbreviations of compound names are given in parenthesis. Uncertainties are 1 standard deviation. <DL indicates below the detection limit.

Molecule	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25
Σn-alkanes	6.2	5.6	5.6	3.1	10.2	1.14	7.9	9.3	3.7	5.9	6.1
CPI	2.8	1.8	1.7	0.7	0.8	0.8	1.5	1.2	0.9	1.6	1.9
C_{max}	C25	C25	C25	C24	C26	C26	C27	C27	C24	C27	C27
17α(H),21β(H)-30-norhopane (29ab)	1.0± 0.7	0.7± 0.1	0.8± 0.4	0.9± 0.8	1.0± 0.7	1.0± 0.4	0.03± 0.05	0.2± 0.03	0.1± 0.06	0.1± 0.09	0.2± 0.2
7α(H),21β(H)-hopane (30ab)	0.9± 0.7	0.6± 0.02	0.5± 0.2	1.1± 1.0	1.0± 0.5	1.3± 0.6	0.03± 0.05	0.1± 0.04	0.2± 0.03	0.09± 0.07	0.1± 0.1
7α(H),21β(H)-22S-homohopane (31abS)	<DL	<DL	<DL	0.5± 0.4	0.7± 0.4	0.7± 0.4	0.03± 0.04	0.07± 0.03	0.1± 0.03	0.06± 0.07	0.07± 0.06
17α(H),21β(H)-22R-homohopane (31abR)	<DL	<DL	<DL	0.4± 0.4	0.5± 0.3	0.8± 0.4	0.03± 0.04	0.06± 0.01	0.09± 0.03	0.05± 0.06	0.06± 0.06
Cholesterol	1.9± 1.0	0.6± 0.2	0.7± 1.2	0.6± 0.4	<DL	3.4± 1.7	4.1± 2.4	3.4± 1.0	6.9± 3.1	7.8± 6.3	5.3± 4.4
Dehydroabietic acid (DHAA)	34.1± 25.8	2.7± 3.8	4.4± 1.4	<DL	4.5± 9.1	8.8± 4.1	<DL	<DL	<DL	<DL	<DL
Dehydroabietic acid methylester (DHAAM)	6.2± 1.2	6.9± 4.6	5.1± 6.2	2.9± 1.9	17± 15.9	1.4± 1.7	<DL	<DL	<DL	<DL	<DL
Mannosan	<DL	<DL	<DL	<DL	<DL	<DL	0.1± 0.14	3.7± 2.3	0.2± 0.5	2.7± 1.6	4.3± 3.8
Levoglucosan	44.6± 30.3	<DL	19.2± 18.8	29.5± 21.2	12.8± 4.1	45.7± 7.3	48± 17.2	98.3± 36.8	86.2± 67.5	130± 67.9	98.7± 84.1
Elemental Carbon (EC)	0.38± 0.11	0.53± 0.04	0.40± 0.37	0.28± 0.24	0.48± 0.06	0.84± 0.40	0.20± 0.10	1.14± 0.33	0.67± 0.29	0.39± 0.12	0.73± 0.13
Organic Carbon (OC)	3.03± 0.56	2.04± 0.52	2.07± 0.71	1.89± 0.60	2.43± 0.42	2.18± 0.86	0.62± 0.60	2.25± 1.10	1.81± 0.66	3.01± 0.71	3.51± 0.19

3.3 Sources of primary $PM_{2.5}$ based on the detected organic compounds

3.3.1 n-alkane concentrations and distribution

The concentration of the targeted n-alkanes is presented in Figure 1, averaged for schools sampled during summer and winter. Vehicles emit alkanes in the range of C_{19-32} (Rogge et al., 1993a). The majority of the detected alkanes were observed in this range, suggesting that this was the main source of alkanes at the schools. Another possible source which has an overlapping alkane distributions are plant waxes, which are associated with alkanes greater than C_{27} (Cass, 1998). From Table S2 and Figure 1 alkanes within this range were also detected, indicating that this was another potential source at all schools. From Figure 1, the schools sampled in summer had a higher abundance of alkanes and a higher association with vehicle emissions than plant wax emissions. This was probably because the schools sampled in summer recorded higher traffic flows (e.g. S15, S19 and S20). At the schools sampled in winter there was a higher abundance of plant wax alkanes ($C_{>27}$) compared to the schools sampled in summer (Figure 1). Plant waxes alkanes can come from either abrasion of vegetation detritus and incomplete biomass burning (Cass, 1998; Pietrogrande et al., 2011; Simoneit, 2002). In Brisbane, most trees are evergreen and winter is the driest time of year, increasing the likelihood of emissions from leaf abrasion. In addition, the practice of prescribed burning of bush land, described in more detail in Section 3.3.3, would also explain the higher abundance of alkanes from plant wax during winter.

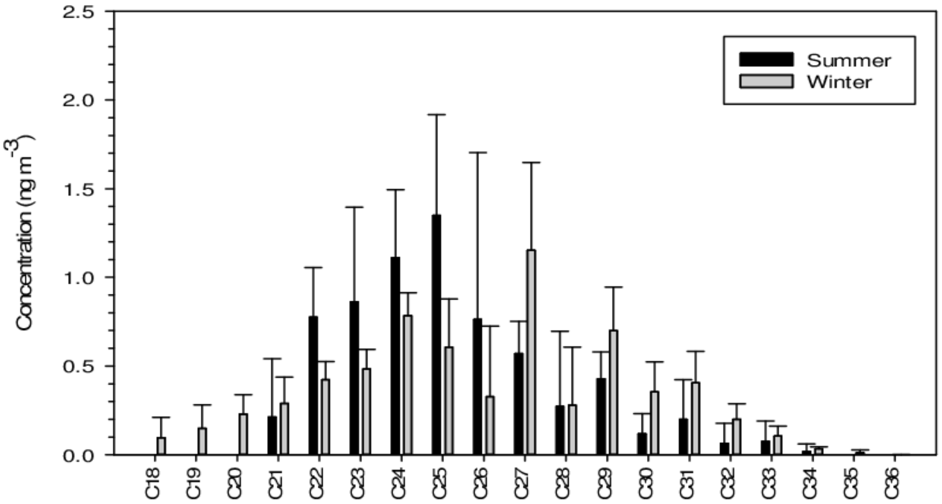

Figure 1: Average summer (n = 23) and winter (n = 20) concentrations of the measured n-alkanes. Variability shown is one standard deviation of the average.

Further differentiation between vehicle emissions and biogenic sources is possible by determining the C_{max}, which refers to the most abundant alkane at each school, from the data in Table 3. At the schools sampled in summer the C_{max} was similar to that expected for gasoline vehicles ($C_{23\text{-}5}$) whereas at schools sampled in the winter the C_{max} was within the range for plant waxes ($C_{>27}$) (Cass, 1998; Rogge et al., 1993a; Schnelle-Kreis et al., 2011). The exception was S23, which had a C_{max} of 24 and this indicates that vehicle emissions were the likely major contributing source of n-alkanes. Carbon preference index (CPI) values, which defined as the ratio of the sum concentration of odd- to even-carbon numbered n-alkanes, has been widely used to distinguish between sources of n-alkanes (Brown et al., 2002). Vehicle emissions are expected to have a ratio around 1 whereas plant waxes are expected to have a ratio >2 (Schnelle-Kreis et al., 2007). In Table 3, the schools with a CPI around 1 were S18, S19, S20, S22 and S23, which were generally the schools beside comparatively higher trafficked roads. However, the CPI of S15-17 would suggest an influence from plant waxes in addition to that from vehicle emissions. Thus, from the n-alkanes it was difficult to distinguish between the contributions of sources, though it is clear that the two main sources were likely to be vehicle emissions and plant

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waxes. Further investigations of the influence of vehicle emissions were possible by analyzing the concentrations and distributions of the hopanes.

3.3.2 Hopane concentrations and distribution

Generally, the same hopanes distribution was found at all of the schools and the average concentration for each hopane is presented in Figure 2. The homohopane isomerization index (HHI, defined as 31abS/31abS+31abR) is about 0.1-0.4 for coal burning and 0.6 for mineral oil emission sources, such as vehicles (Oros and Simoneit, 2000; Schnelle-Kreis et al., 2011). For the schools where these homohopanes were detected, the HHI ranged from 0.5 - 0.6, indicating vehicle emissions were the source. This was expected as very little coal and oil burning for domestic heating occurs in Brisbane and this may explain why the other targeted hopanes were below the detection limit of majority samples (See Figure 2). The hopane concentrations were observed to be higher at the schools sampled in summer (S15-20, See Table 2 for selected hopanes) and is the reverse of what was previously observed in Europe (Schnelle-Kreis et al., 2005). This was likely due to the lower emissions of hopanes from coal burning as well as the observed increased contribution from vehicle emissions at the schools sampled in summer. Therefore, based on the hopanes detected the main source of fossil fuel combustion at the schools was vehicle emissions.

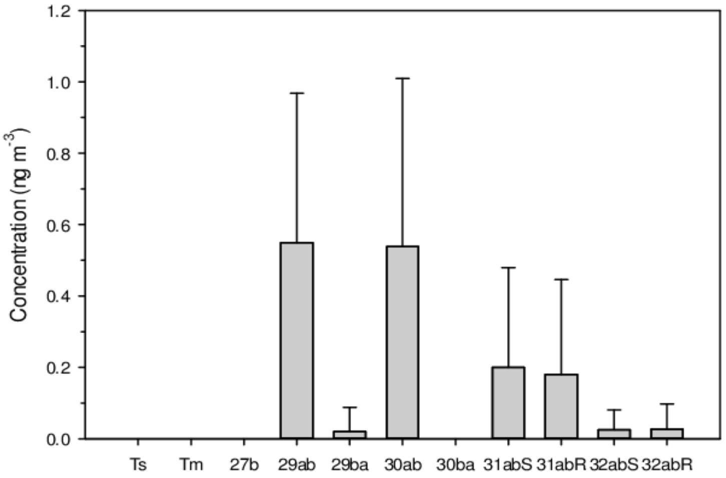

Figure 2: Average concentration of analyzed hopanes across all schools. Variability shown is one standard deviation of the average. Note the following abbreviations used not described in the text: Ts (18α(H)-22,29,30-trisnorneohopane), Tm (17α(H)-22,29,30-trisnorhopane), 27b (17β(H)-22,29,30-trisnorhopane), 30ba (17β(H),21α(H)-hopane), 32abS (17α(H),21β(H)-22S-bishomohopane) and 32abR (17α(H),21β(H)-22R-bishomohopane).

3.3.3 Biomass burning tracers

A number of biomass burning tracer compounds were detected in this study, and include the anhydrous sugar, levoglucosan, galactosan, mannosan (Qadir et al., 2013; Robinson et al., 2006a; Simoneit, 2002) and the resin acid DHAA and DHAA-ME (Rogge et al., 1998). DHAA is also a constituent of vehicle tyres, indicating another possible source at the schools (Rogge et al., 1993b) (Sheya, 2002). As levoglucosan was generally the most abundant compound detected at most of the schools (Table 3), it indicates that biomass burning was a significant source. Schools sampled in the summer generally had a lower concentration than the schools sampled in winter, with the averages of 27.6±22.4 and 94.6±60.3 ng m^{-3} for summer and winter, respectively. By comparison, using the same analytical technique, the mean levoglucosan concentrations were higher in Augsburg, Germany compared to the current study at 112±84 and 337±174 ng m^{-3} for summer and winter, respectively (Pietrogrande et al., 2011). The lower concentrations in the current study are likely to be due to the warmer climate in Brisbane and the resulting low levels of domestic wood burning for heating.

Distinct seasonal trends were observed between the schools sampled in summer and winter in the concentrations and distributions of the biomass burning tracers. Schools sampled in winter recorded higher concentrations of levoglucosan and mannosan, compared to schools sampled in summer, whereas the schools sampled in summer had higher concentrations of DHAA (Table 3). All of these seasonal differences were statistically significant ($p<0.05$). The higher concentrations of the biomass burning tracers, levoglucosan and mannosan in winter is expected in Brisbane due to the influence of prescribed burning of bushland surrounding the city during the winter to reduce the risk of summer bush fires. Prescribed burning typically occurs during July-August, which was when the highest concentration of levoglucosan and mannosan were observed (Table 3). The levoglucosan detected at the schools sampled in the summer are likely to be from a different wood burning source as unlike at the schools sampled in winter (Table 3), these schools recorded concentrations of DHAA above the detection limit. DHAA is emitted only from softwood combustion (specifically pine) unlike levoglucosan which is emitted by combustion of all forms cellulose containing materials (Pietrogrande et al., 2011; Robinson et al., 2006a; Rogge et al., 1998). This suggests that in the summer there is a different source of biomass burning, possibly related to domestic wood burning such as from barbeques. In the previous section, higher contributions from vehicle emission at schools sampled in summer were observed and another possible source of DHAA is vehicle tyres wear. Thus, traffic emissions may have been a contributing source to the observed levels of DHAA at the schools along with domestic wood burning barbeques.

3.4 Source apportionment using PMF

To apportion the contributions of the different sources of primary organic aerosols identified at each school to the OC fraction, PMF was applied to the dataset. Solutions with 3-5 factors were investigated and the three factor solution was rejected as it could not separate out the cooking and biomass burning factors. The five factor solution was not used due to splitting of the vehicle emissions source factor into unrealistic factors. Therefore the four factor solution was found to best represent the data as it gave realistic source profiles related to distinct primary sources. Source profiles are given in Figure 3 and were assigned to biomass burning, cooking, vehicle and plant wax emissions based upon the high concentrations of known tracer molecules for these sources. The contributions of each identified source factors to the OC at all schools are given in Figure 4 and the factors will be discussed in order of their contribution to the OC rather than factor number.

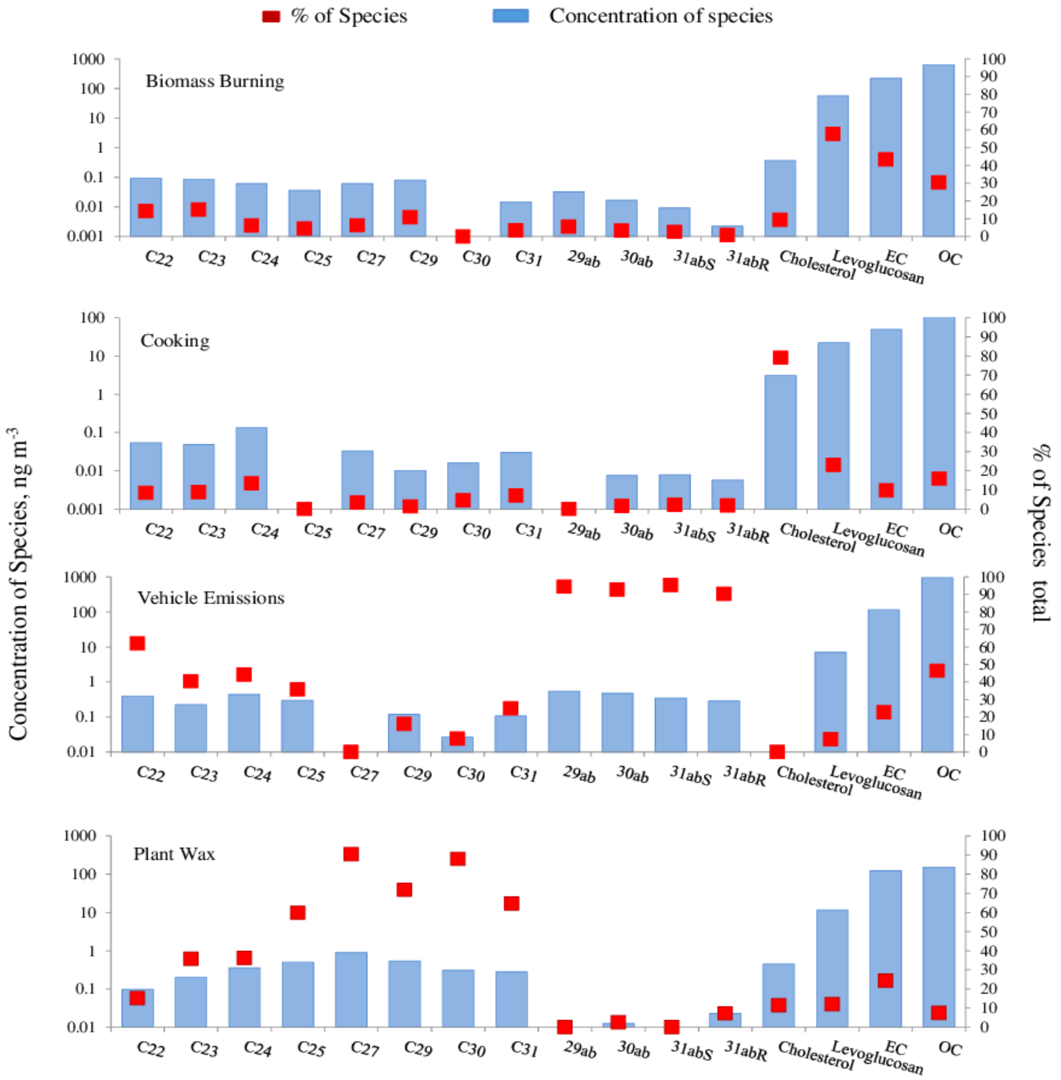

Figure 3: Source factor profiles from the positive matrix factorization (PMF) analysis using EPA-PMF3.0 model. Bars represent mass concentration while the squares indicate the percentage contribution.

The major source, vehicle emissions (See Figure 4), was characterized by the $C_{20\text{-}25}$ alkanes and the hopanes 29ab, 30ab, 31abS and 31abR. C_{20} and $C_{23\text{-}5}$ alkanes have previously been shown to be associated with diesel and gasoline vehicle emissions (Rogge et al., 1993a). This together with the fact that the hopanes determined in Section 3.2.2 were deemed to be from fossil fuel combustion, points to vehicle emissions as the source. The HHI for this factor was 0.85 and in the range expected for vehicle emissions, further indicating vehicle emissions as a source. This factor contributed to 45% of the OC at the schools and was therefore the main source in our study. The factor was only somewhat correlated with the traffic counts beside the schools (r^2 of 0.3), probably due to the multiple variables that contribute to the observed levels of vehicle emissions at the schools (Crilley et al., 2013). However, it was observed that with the exception of S18 (Table 2), the schools with the highest contributions from vehicle emissions (S15, S17, S19 and S20, Figure 4) recorded high traffic counts. Unlike the other schools, which were in suburban areas, S18 is in an inner-city location and this may explain the high levels for this factor

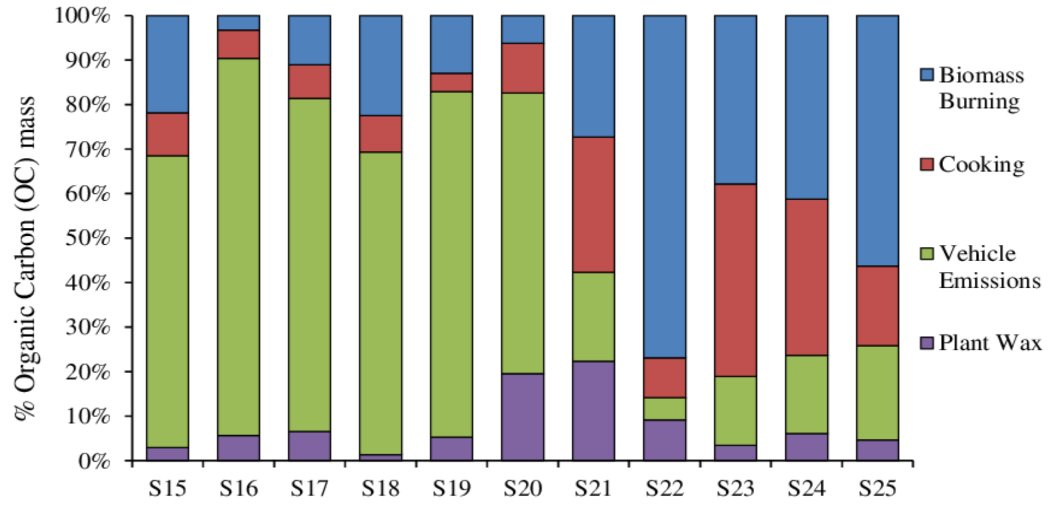

Figure 4: Percentage of contributions of the PMF source factors to organic carbon (OC) mass at the 11 different schools

The first factor was assigned to biomass burning as it was characterized by high contributions of levoglucosan, the molecular marker for biomass burning (Qadir et al., 2013; Robinson et al., 2006a; Simoneit, 2002). The OC/EC ratio for this factor was 2.8, which is lower than the ratio of OC/EC from previous study held in Australia (Keywood et al., 2011). However, this could be explained by higher contribution of EC, which is a marker for vehicle emissions (Sonntag et al., 2012), to the PMF profile. The biomass burning factor was the second largest source overall during the study, accounting for 29% of the OC (Figure 4). From Figure 4, the highest contributions were as expected, found during the winter (S22, S24 and S25) primarily due to the practice of prescribed burning of bushland surrounding Brisbane.

The next source, which accounted for 16% of the OC was characterized by cholesterol. As cholesterol is a known tracer for meat cooking (Kleeman et al., 2008), this source was assigned to meat cooking emissions. Cooking emissions are increasingly being identified as a significant urban source (Mohr et al., 2012; Robinson et al., 2006b) and the observed high contributions may be indicative of localized emissions from school canteens. This is illustrated at S24 where the high concentrations (Figure 4) were likely due to a school barbeque event that occurred on one of the sampling days. In addition, S23 had high concentration of meat cooking emissions because it is located near a large

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number of restaurants. This probably suggests that apart from the school canteen, there was an additional source at the school.

High contributions of the alkanes C_{25}, C_{27} and $C_{29} – C_{31}$ characterized the last factor, which was assigned to plant waxes. Plant waxes particles can enter the atmosphere from either leaf abrasion (Rogge et al., 1993c) or incomplete biomass burning (Simoneit, 2002). Both of these source pathways were likely as the highest contributions were observed at schools (S20, S21 and S22) sampled during the driest time of the year and schools that recorded strong biomass burning influences (Figure 4). This factor accounted for 7% of the OC and was the smallest contributing source of primary aerosols at the schools.

As the schools selected for this study were not close to any other large source of air pollution other than road traffic, the main source of primary organic aerosol was hypothesized to be vehicle emissions. This hypothesis was confirmed based upon the PMF analysis on selected tracer organic molecules (Figure 4). The lower contribution from biomass burning source to OC mass at S16-S21 (Figure 4) was due, in part, to the sampling at these schools occurring when the contributions of biomass burning from prescribed burning were at a minimum. Generally, year-round vehicle emissions were found to have a largest overall contribution to the OC mass at the schools. Previous work on $PM_{2.5}$ in urban environments using an organic molecular marker approach also found that vehicle emissions rather than wood combustion were the largest primary source of $PM_{2.5}$ (Green et al., 2013; Wang et al., 2012). Unlike in the current work where prescribed fires in surrounding bushland were the source of biomass burning, the wood combustion was attributed primarily to residential heating in those studies (Green et al., 2013; Wang et al., 2012).

4.0 Conclusions

Selected organic molecular markers were quantified in order to apportion the contributing sources of primary organic aerosols to children's exposure of $PM_{2.5}$ at urban schools, with vehicle emissions hypothesized to be the largest contributing source. Using PMF, four source factors were identified and assigned to vehicle emissions, biomass burning, meat cooking and plant wax emissions. Vehicle emissions, which were characterized by C_{20-25} alkanes and the observed hopanes accounted for 45% of the overall OC, with schools having the highest traffic counts recording higher contributions. Biomass burning recorded high contribution to the OC (29%) and a seasonal trend that peaked in winter due to prescribed burning in bush land around Brisbane was also observed. For the same reasons, plant wax alkanes demonstrated a similar seasonal trend, though this source only accounted for a small fraction (7%) of the OC. Cooking emissions accounted for 16% of the OC, with a school nearby a restaurant precinct recording high contributions. Therefore, based upon the targeted organic molecular markers, vehicle emissions were the major source of organic aerosols at the schools studied, confirming the hypothesis. The second largest contribution was from a more regional source, in this case biomass burning as a result of controlled burning of bushland surrounding Brisbane to reduce the risk of summer bushfires.

Controlled burning of bushland is common practice near urban areas in Australia as well as in other countries that are affected by wild bush or forest fires such as the U.S.A and Mediterranean countries. Thus the significant influence of biomass burning from both controlled and wild fires that was observed in the results from this study is potentially applicable to other urban areas in Australia and other countries. Another notable aspect of the results was the large contribution from meat cooking emissions, possibly due to activities at the schools. This result warrants further investigations to determine the full impact of meat cooking emissions at schools. Finally, although vehicle emissions were identified as a major source in this study, it is not necessarily the only major source of pollution in urban areas, as only a subset of organic compounds were analyzed in this work. Overall, the results from this study point to the influence of both local (traffic) and regional (biomass burning) sources of primary organic aerosols on the levels of ambient particles that children are exposed at schools. This has implications for potential control measures for mitigating exposure at schools.

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Supplementary Material

Paper: Identification of the sources of primary organic aerosols at urban schools: a molecular marker approach

Table S1: Detection limits for the analysed hopane and polar compounds.

Compound	Detection Limit (ng/m^3)
18α(H)-22,29,30-trisnorneohopane (Ts)	0.05
17α(H)-22,29,30-trisnorhopane (Tm)	0.05
17β(H)-22,29,30-trisnorhopane (27b)	0.05
17α(H),21β(H)-30-norhopane (29ab)	0.05
17β(H),21α(H)-30-norhopane (29ab)	0.05
17α(H),21β(H)-hopane (30ab)	0.05
17β(H),21α(H)-hopane (30ba)	0.05
17α(H),21β(H)-22S-homohopane (31abS)	0.05
17α(H),21β(H)-22R-homohopane (31abR)	0.05
17α(H),21β(H)-22S-bishomohopane	0.05
17α(H),21β(H)-22R-bishomohopane	0.05
Cholesterol	0.05
Dehydroabietic acid (DHAA)	0.10
Dehydroabietic acid methylester (DHAAM)	0.02
Mannosan	0.10
Levoglucosan	0.10

Figure S1: Map of Brisbane city indicating the locations of sites and potential sources. Green shaded areas represent bushland, blue shaded areas the ocean/lakes and major roads are shown. CBD indicates the central business district.

Table S2: Detection Limits (DL) and average concentrations of the n-alkanes at the schools. Abbreviations of compound names are given in parenthesis. Uncertainties are 1 standard deviation. <DL indicates below the detection limit.

Compound	**DL, ng/m^3**	**S15**	**S16**	**S17**	**S18**	**S19**	**S20**	**S21**	**S22**	**S23**	**S24**	**S25**
Octadecane (C$_{18}$)	0.05	<DL	<DL	<DL	<DL	<DL	<DL	0.2±0.3	0.3±0.5	0.03±0.05	<DL	0.02±0.04
Nonadecane (C$_{19}$)	0.05	<DL	<DL	<DL	<DL	<DL	<DL	0.03±0.1	0.3±0.1	0.06±0.1	0.07±0.06	0.3±0.3
Eicosane (C$_{20}$)	0.05	<DL	<DL	<DL	<DL	<DL	<DL	0.2±0.2	0.4±0.2	0.1±0.03	0.2±0.01	0.3±0.2
Heneicosane (C$_{21}$)	0.05	<DL	<DL	<DL	<DL	0.6±1.3	<DL	0.2±0.2	0.5±0.3	0.2±0.02	0.2±0.09	0.4±0.2
Docosane (C$_{22}$)	0.05	0.6±0.43	0.5±0.02	0.7±0.3	0.7±0.09	1.1±0.6	0.3±0.5	0.3±0.2	0.5±0.08	0.4±0.09	0.5±0.08	0.5±0.3
Tricosane (C$_{23}$)	0.05	1.7±0.3	0.6±0.3	0.4±0.02	0.3±0.1	1.1±0.5	0.1±0.2	0.5±0.4	0.5±0.1	0.3±0.09	0.5±0.1	0.6±0.3
Tetracosane (C$_{24}$)	0.05	1.0±0.7	1.0±0.5	0.8±0.2	0.7±0.2	1.6±0.6	0.4±0.7	0.7±0.8	0.8±0.4	0.7±0.5	1.0±0.7	0.8±0.5
Pentacosane (C$_{25}$)	0.05	1.9±0.1	1.4±1.0	1.1±0.3	0.4±0.1	1.7±0.8	0.1±0.2	0.7±0.9	1.0±0.1	0.3±0.1	0.5±0.2	0.6±0.6
Hexacosane (C$_{26}$)	0.05	<DL	<DL	0.2±0.4	0.4±0.5	2.0±0.8	<DL	0.5±0.8	1.0±1.9	0.2±0.4	<DL	<DL
Heptacosane (C$_{27}$)	0.05	0.6±0.1	0.5±0.2	0.5±0.1	0.3±0.08	0.8±0.5	0.1±0.2	1.7±2.4	1.5±0.3	0.5±0.4	1.0±0.7	1.1±1.1
Octacosane (C$_{28}$)	0.05	<DL	<DL	<DL	<DL	0.8±0.7	<DL	0.4±0.7	0.8±1.0	0.2±0.4	<DL	<DL
Nonacosane (C$_{29}$)	0.05	0.3±0.5	0.5±0.2	0.7±0.5	0.3±0.1	0.4±0.3	0.2±0.5	0.9±1.1	0.8±0.3	0.3±0.2	0.8±0.6	0.6±0.4
Triacontane (C$_{30}$)	0.05	<DL	0.2±0.05	0.3±0.1	<DL	0.1±0.2	<DL	0.6±0.9	0.4±0.2	0.2±0.07	0.4±0.3	0.3±0.3
Hentriacontane (C$_{31}$)	0.05	<DL	0.4±0.3	0.6±0.5	<DL	0.1±0.3	<DL	0.7±1.1	0.4±0.1	0.2±0.07	0.4±0.2	0.3±0.2
Dotriacontane (C$_{32}$)	0.05	<DL	0.3±0.1	0.1±0.1	<DL	<DL	<DL	0.3±0.5	0.2±0.1	0.1±0.02	0.2±0.09	0.2±0.1
Tritriacontane (C$_{33}$)	0.05	<DL	0.2±0.3	0.2±0.4	<DL	<DL	<DL	0.06±0.1	0.1±0.02	0.05±0.06	0.2±0.1	0.1±0.03
Tetratriacontane (C$_{34}$)	0.05	<DL	0.1±0.1	<DL	<DL	<DL	<DL	0.04±0.05	0.03±0.02	0.04±0.05	0.05±0.05	0.02±0.03
Pentatriacontane (C$_{35}$)	0.05	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.02±0.02	0.01±0.03	0.03±0.06	<DL
Hexatriacontane (C$_{36}$)	0.05	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.03±0.06	<DL	<DL	<DL