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ICARUS

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Application of source apportionment methods to identify emission sources with the help of ambient air quality measurements in six European cities

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Finally, I would like to thank my German family, my neighbours and friends in Stuttgart for their unconditional friendship during these years.

Stuttgart, January 2019 Miriam Chacón Mateos

Task Description

Within the EU project ICARUS different source apportionment methods will be applied to identify different emission sources and determine the ratio of these sources compared to the total load of all air pollutants. Source apportionment will also allow to better understand the relative effect of regional scale air quality to the urban scale; to estimate this interaction precisely will affect the efficacy of the proposed mitigation and abatement measures. First, this information can be used to evaluate emission and atmospheric transport modelling by comparing model results with results of the source apportionment, thus detecting source specific deviations. Secondly, it can be used as a shortcut for estimating effects of measures on concentrations without using transport models. For example, if the share of local wood firings on concentrations of PM2.5 is x %, then a reduction of y % on emissions of wood firings will result in a reduction of (x*y)/100 % of the concentration.

Many different source apportionment methods are described in the literature and were tested and applied in different research projects in the past. These models are among others: receptor models (RMs), such as Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) as well as the Lenschow approach. Assessment of chemical mass balance rely on air pollution monitoring data coming from the regular monitoring networks, remote sensing (satellite and aerial) data, as far as available data from measurement campaigns or eventually modelled data in order to fill data gaps. A wide variety of pollutants (e.g. CO, NO_x, O_3, BC, SO_2, benzene, BaP) should be included in the approach beside chemical speciation (ions, heavy metals, OC/EC) of Particulate Matter samples.

The aim of this work is to apply source apportionment methods on a set of data. This data set was compiled during two sampling campaigns which took place in a summer and winter in six European cities in the year 2017. In each city three measurement sites were selected, a rural background site, an urban background site and a site near an urban traffic hotspot, as traffic is the main source of air pollution in many cases. Within the summer and winter measurement campaigns, up to 31 daily PM2.5 samples were collected at the three sites simultaneously. After that analysis of the PM composition were done, by applying different analysis methods to determine PAHs (polycyclic aromatic hydrocarbons), OC/EC (organic/elemental carbon), BC (black carbon), anions, cations and heavy metals. Two source apportionment methods should be applied to the entire data set for all six European cities: the Lenschow approach and the Positive Matrix Factorization (PMF).

The works to be done are the following:

a) Literature research of the different source apportionment methods.
b) Detailed description of the *Lenschow approach* and the *Positive Matrix Factorization*.
c) Application of the approaches on the data set of the ICARUS project.
d) Comparison of the results of these two approaches to the results of the application of other approaches (PMF – Positive Matrix Factorization and PCA – Principal Component Analysis) of project partners on the same data set.

The Master Thesis is supervised by Dr.-Ing. *Ulrich Vogt*. The information sheet on the conduction and the production of a project at IFK shall be respected.

Start of the project: 06.08.2018
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(Apl. Prof. Dr.-Ing. Uwe Schnell)

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Kurzfassung

Die Quantifizierung der Beiträge zu den Schadstoffquellen ist ein Schlüsselelement für die Umsetzung der Richtlinien über die Luftqualität (2008/50/EG und 2004/107/EG). Im Rahmen des ICARUS-Projekts wurde die Quellenzuordnung für PM2.5 in sechs europäischen Städten (Athen, Brno, Ljubljana, Madrid, Thessaloniki und Stuttgart) anhand von Datensätzen von Messungen in zwei verschiedenen Jahreszeiten (Sommer und Winter) und zwei Modellierungswerkzeugen bewertet: dem *Lenschow Approach* und der *Positive Matrix Factorization*. Um die Zuverlässigkeit und Robustheit der Ergebnisse zu erhöhen, wurde ein Vergleichs mit zwei Rezeptormodellen für die gleichen Datensätze durchgeführt: die *Principal Component Analysis* und das *Positive Matrix Factorization Model*, das von einer anderen Institution betrieben wird. Es wurde festgestellt, dass der *Lenschow Approach* nicht die gleichen Ergebnisse zeigt wie die Rezeptormodelle und daher nicht zur Entwicklung von Strategien für die städtische Luftqualitätsplanung, sondern nur als qualitative Methode verwendet werden kann. Der Vergleich der Rezeptormodelle wurde zur Validierung der Ergebnisse genutzt. Fünf Quellen wurden als Hauptquellen für PM2.5 in allen teilnehmenden Städten ermittelt, nämlich Verkehr, sekundäre anorganische Aerosole (Nitrate und Sulfate), Aufwirbelung des Bodenstaubes, Heizsysteme (Biomasseverbrennung und/oder Heizölverbrennung) und Industrie. Geographische und saisonale Schwankungen wurden beobachtet, insbesondere bei Heizungen als Emissionsquelle. Auf Basis dieser Ergebnisse sollten lokale Luftqualitätsmaßnahmen zur Bekämpfung der Luftverschmutzung konzipiert werden.

Abstract

The quantification of pollution sources contributions is a key element for the implementation of the Directives on Air Quality (2008/50/EC and 2004/107/EC). Within the ICARUS project, the source apportionment of PM2.5 in six cities of Europe (Athens, Brno, Ljubljana, Madrid, Thessaloniki and Stuttgart) was assessed using datasets of measurements made in two different seasons (summer and winter) and two modelling tools: the *Lenschow approach* and the *Positive Matrix Factorization*. In order to increase the reliability and robustness of the results, an inter-comparison exercise was carried out with two receptor models for the same datasets: the *Principal Component Analysis* and the *Positive Matrix Factorization* model run by a different institution. It was observed that the *Lenschow approach* does not show the same results as the receptor models and therefore cannot be used to design strategies for urban air quality planning but just as a qualitative method. The comparison of the receptor models had led to the validation of the results. Five sources have been found to be the main sources of PM2.5 in all the participating cities, namely, traffic, secondary inorganic aerosols (nitrates and sulphates), resuspension of soil dust, heating systems (biomass burning and/or fuel oil combustion) and industry. Geographical and seasonal variation have been observed, especially for heating sources hence, air quality measures at local scale should be designed for the abatement of air pollution.

Table of Contents

List of Abbreviations

Abbreviation	Meaning
2,3,5- trimethylN	2,3,5- trimethylnaphthalene
ANN	Artificial Neural Networks
APCFA	Absolute principal component factor analysis
AUTH	Aristotelio Panepistimio Thessalonikis
B(a)P	benzo(a)pyrene
B(a)A	benzo(a)anthracene
B(b)F	Benzo(b)fluoranthene
B(k)F	Benzo(k)fluoranthene
B(ghi)P	Benzo(ghi)perylene
B(ghi)F	Benzo(ghi)fluoranthene
B(j)F	Benzo(j)fluoranthene
B(e)P	Benzo(e)pyrene
BC	Black carbon
CLRTAP	Convention on Long-Range, Transboundary Air Pollution
CMB	Chemical Mass Balance
COPREM	Constrained physical receptor model
CPF	Conditional probability function
DiB(ac)A	Dibenzo(ac)anthracene
DiB(ah)A	Dibenzo(ah)anthracene
FA	Factor analysis
EU	European Union
EPA	Environmental Protection Agency
EX	Traffic exhaust sources
GHGs	Greenhouse Gases
ICARUS	Integrated Climate forcing and Air Pollution Reduction in Urban Systems.
IP	Indeno(1,2,3-c,d)pyrene
ISCIII:	Instituto De Salud Carlos III
JSI	Institut Jozef Stefa

Abbreviation	**Meaning**
ME	Multilinear engine
MU	Masarykova univerzita
NCSRD	National Center for Scientific Research "Demokritos"
NFR	Nomenclature for Reporting
NMVOC	Non-methane Volatile Organic Compounds
NEX	Non-exhaust traffic emissions
OC/EC	Organic carbon/Elemental carbon
OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
PCA	Principal Component Analysis
PM	Particulate matter
PM10	Particles which pass through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter
PM2.5	Particles which pass through a size-selective inlet with a 50 % efficiency cut-off at 2,5 µm aerodynamic diameter
PMF	Positive Matrix Factorization
POA	Primary Organic Aerosols
POC	Primary Organic Carbon
PSCF	Potential Source Contribution Function
RB	Regional background
RMs	Receptor Models
SA	Source Apportionment
SES	Socio-economic Status
S/N	signal-to-noise ratio
SOA	Secondary Organic Aerosols
SOC	Secondary Organic Carbon
T	Traffic
UB	Urban background
USTUTT	Universität Stuttgart
WHO	World Health Organization
WP	Work Package

1 Scope: ICARUS Project Horizon 2020

ICARUS is a four years project funded in the frame of Horizon 2020 which is made up of 18 Partner Institutions from 9 European countries all with multidisciplinary expertise in intersecting and complimentary research areas related to the climate and the environment and their interactions with health and wellbeing. The high scientific quality of the ICARUS team is based on the extensive and long-term experience of the partners, which include leading scientists and risk health research institutes in Europe (ICARUS Horizon 2020, 2016).

ICARUS will develop a first-of-a-kind transdisciplinary methodology and toolkit for integrated impact assessment so that air quality improvement, climate change mitigation and health promotion can be evaluated efficiently in key sector policies. Innovative tools for urban impact assessment leading to the design and the implementation of win-win strategies to improve the air quality and reduce the carbon footprint in European cities will be developed.

State-of-the art technologies are being used for fusing the necessary environmental and ancillary information to allow cost-effective air pollution monitoring and assessment. The tools developed will allow the analytical accounting of the main emission sources and the creation of precise and updated emission inventories. An integrated approach is used for air pollution monitoring combining ground-based measurements, atmospheric transport and chemical transformation modelling and air pollution indicators derived from satellite, airborne and personal remote sensing. Thus, air quality is readily assessed across different spatial scales in the participating cities (ICARUS Horizon 2020, 2016).

Agent-based modelling will be used to capture the interactions of population, industries and service providers in response to the policies considered in the project. Thus, social and cultural factors, socio-economic status (SES) and societal dynamics will be explicitly considered to assess the overall policy impact. The findings will be translated into a web-based guidebook for sustainable air pollution and climate change governance in all EU cities.

ICARUS will develop a vision of a future green city: a visionary model that will seek to minimize environmental and health impacts. Transition pathways will be drawn that will demonstrate how current cities could be transformed towards cities with close to zero or negative carbon footprint and maximal wellbeing within the next 50 years. To raise citizen awareness regarding the impacts of their activities on air pollution and climate forcing and increase societal acceptance of emission reduction policies, a web- and smartphone/tablet-based tool will be developed to inform citizens about how their life style affects their carbon footprint and the health impacts of their actions/consumer choices (ICARUS Horizon 2020, 2016).

The ICARUS methodology and toolkit is currently being applied in nine EU cities of variable size, socio-economic condition and history. Technological and non-technological measures and policy options will be analysed and proposed to the responsible authorities for air pollution and/or climate change at the city level. Based on the advanced monitoring and assessment tools outlined above, a cloud-based solution will be developed to inform citizens of environment-conscious alternatives that may have a positive impact on air quality and carbon footprint and finally on their health and motivate them to adopt alternative behaviours (ICARUS Horizon 2020, 2016).

The present work forms part of the Work Package 3 (WP3), “Integrated atmospheric modelling for connecting pressures to the environment to concentrations at the regional and urban scales” and the subtask 3.2, “Source Apportionment”.

The objective of this work is to apply source apportionment methods on a set of data. This data set was compiled during two sampling campaigns which took place in a summer and winter in six European cities in the year 2017, namely, Athens, Brno, Ljubljana, Madrid, Stuttgart and Thessaloniki. In each city three measurement sites were selected, a rural background site, an urban background site and a site near a traffic hotspot. Within the summer and winter measurement campaigns, up to 31 daily PM2.5 samples were collected at the three sites. After that, the analysis of the PM2.5 composition was done to determine PAHs (polycyclic aromatic hydrocarbons), OC/EC (organic/elemental carbon), anions, cations and heavy metals. Two source apportionment methods were applied to the entire data set for the six European cities. The Lenschow approach and the so-called PMF *(*Positive Matrix Factorization*)*. The results of this work will be used to validate the results of the PCA (Principal Component Analysis) and the PMF models used for the WP3 subtask 3.2.

2 Introduction

2.1 Definition of Source Apportionment

Source Apportionment (SA) is the practice of deriving information about pollution sources and the amount they contribute to ambient air pollution levels (Belis, 2013).

Information on pollution sources is essential in the design of air quality policies and, therefore, SA is required explicitly or implicitly for the implementation of the Air Quality Directives. The most relevant reasons for a source apportionment study are namely (Belis, 2013):

- The design of air quality actions (Dir. 2008/50/EC and Dir. 2004/107/EC arts. 23 and 24).
- Identifying causes of exceedances of guideline and limit values in the ambient air.
- Identifying the contribution from other countries (transboundary pollution – Dir. 2008/50/EC art.25).
- Identifying the contribution from different geographic areas within a country.
- Applying for postponement of attainment (2008/50/EC art.22).
- Assessing effectiveness of abatement measures.
- Detracting natural sources or road salting and sanding in winter from PM (Dir. 2008/50/EC art. 21).
- Refining emission inventories.

Different approaches are used to determine and quantify the impacts of air pollution sources on air quality. Commonly used SA techniques are (Belis et al, 2014):

- **Exploratory methods**, which use simple mathematical relationships and a number of assumptions to achieve a preliminary estimation of the source contribution. Examples of this category are the Enrichment factor, the Incremental approach and the Lenschow approach.
- **Emission inventories**, which are detailed compilations of the emissions from all source categories in a certain geographical area and within a specific year. Emissions are estimated by multiplying the intensity of each relevant activity (activity rate) by a pollutant-dependent proportionality constant (emission factor).
- **Inverse modelling**, in which air quality model parameters are estimated by fitting the model to the observations. The inverse technique consists of a least squares optimisation

with an objective function defined as the sum of squared deviations between modelled and observed concentrations.

- **Artificial Neural Networks** (ANN), which are sets of interconnected simple processing elements (artificial neurons) which can exhibit complex global behaviour. In order to produce a desired signal flow, algorithms designed to modulate the weights of the connections in the network are applied.
- **Lagrangian models** use a moving frame of reference to describe the trajectories of single or multiple particles as they move in the atmosphere.
- **Gaussian plume models** assume that turbulent dispersion can be described using a Gaussian distribution profile. This type of model is often used to estimate emissions from industrial sources.
- **Eulerian models** encompass equations of motion, chemistry and other physical processes that are solved at points arranged on a 3D grid.
- **Receptor models** (RMs) estimate pollution sources contributing to the ambient air in a specific site using multivariate statistical analysis. RMs solve a mass balance equation using the concentration of pollutants measured at the receptor and the sources relative chemical compositions, also known as fingerprints.
  (Karagulian, 2012).

The models above described can be classified into three main approaches: emission inventories, source-oriented models or dispersion models (used to refer Lagrangian, Gaussian and Eulerian) models and receptor-oriented models.

As it is shown in Figure 2.1, RMs focus on the properties of the ambient environment at the point of impact, as opposed to the source-oriented dispersion models which account for transport, dilution, and other processes that take place between the source and the sampling or receptor site. Source-oriented models estimate source contributions by imitating the physical and chemical processes in the atmosphere based on the input from emission inventories and meteorological data (Karagulian, 2012).

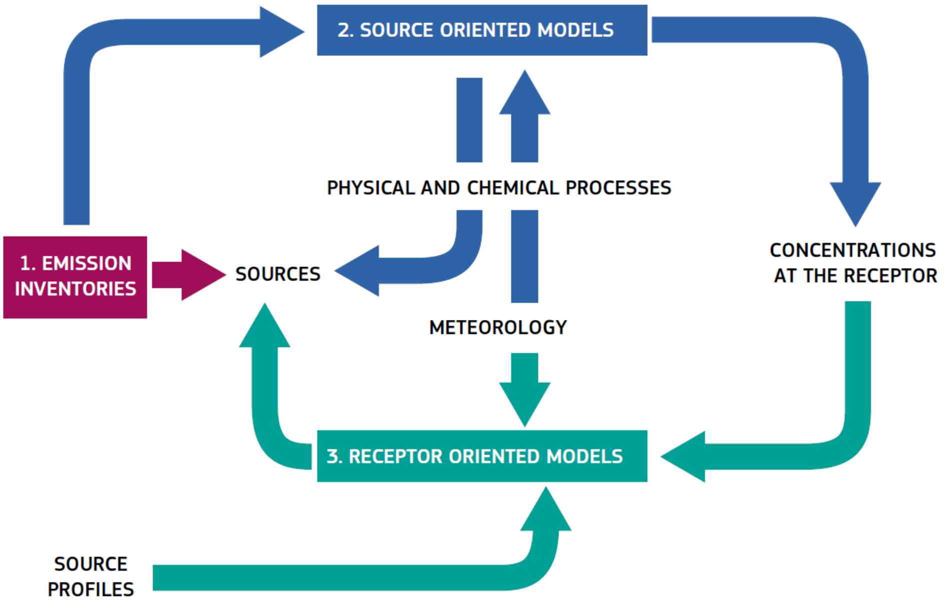


Figure 2.1. Schematic representation of the different methods for source identification.

2.2 Receptor models

Receptor models are mathematical approaches for quantifying the contribution of sources to samples based on the composition or fingerprints of the sources. The composition or speciation is determined using analytical methods appropriate for the media, and key species or combinations of species are needed to separate impacts. A dataset can be viewed as a data matrix X of i by j dimensions, in which i number of samples and j measured chemical species. The goal of receptor models is to solve the chemical mass balance (CMB) between measured species concentrations and source profiles, as shown in Equation 2.1,

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad \text{Equation 2.1}$$

where p is the number of factors, g_{ik} is the contribution of the source k to the sample i, f_{kj} the concentration of the j specie in the source k and e_{ij} the residual term for each sample/specie (i.e the difference between the measured and the fitted value) (Norris, 2014).

In order to find the solution, a dataset with a rather large amount of data consisting of chemical constituents (such as elemental concentrations) gathered from a number of observations (samples) is required. The larger the data matrix, the higher the chances that the model will identify distinct factors (sources). Johnson et al. (2011) claim that at least 50 chemically characterised ambient samples are required for running multivariate models. However, at least 100 samples of 24-hour data of at least 20 species are recommended by Brown and Hafner (2005).

If the number and nature (composition profiles/fingerprints) of the sources in the study area are known (f_{kj}), then the only unknown term of Equation 2.1 is the mass contribution of each source to each sample, g_{ik}. The problem is typically solved using an effective-variance least-squares approach that is now generally referred to as the chemical mass balance (CMB) model. Many models and methodologies have been developed and are still under continuous evolution. The main types of RMs are presented in Table 2.1 (Belis et al, 2014).

Table 2.1 Types of Receptor Models.

Type	**Example**
Chemical Mass Balance	EPA CMB 8.2
Eigenvector-based models	PCA
	UNMIX
Factor analysis without constrains	FA
	APCFA
Positive Matrix Factorization	EPA PMF 5.0
Hybrid trajectory-based models	CPF
	PSCF (Openair package for R)
Hybrid expanded models	PMF solved with ME-2
	COPREM

CMB: chemical mass balance, PCA: principal component analysis, FA: factor analysis, APCFA: absolute principal component factor analysis, PMF: positive matrix factorization, ME: multilinear engine, CPF: conditional probability function, PSCF: potential source contribution function, COPREM: Constrained physical receptor model.

The required information about the sources varies among the different approaches as can be seen in

Figure 2.2 (Belis et al, 2014).

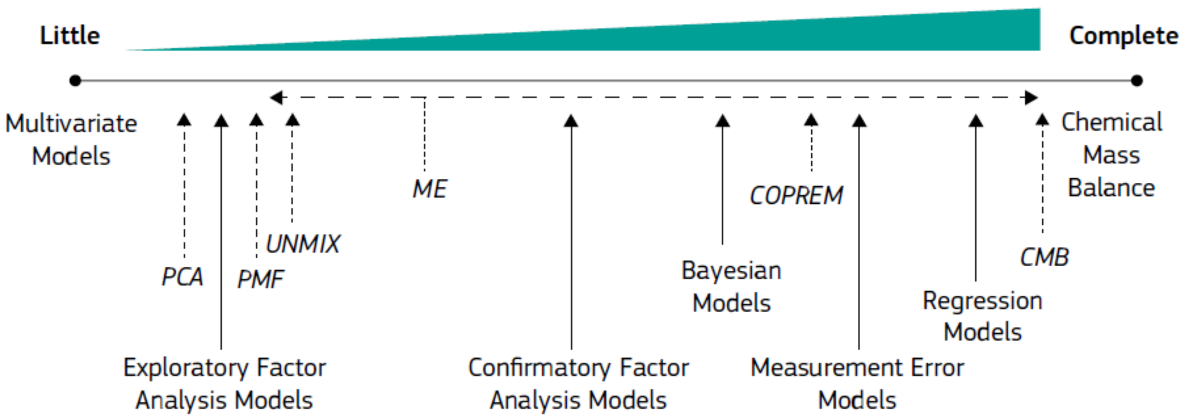


Figure 2.2. Knowledge required about pollution sources prior to receptor modelling (Belis et al, 2014).

Within the ICARUS project, approaches that require less information about the emission sources have been used, namely PCA and PMF. The main advantage of these methods is that little information about emission sources is needed, and sources or processes so far not registered in an emission inventory may be detected. On the other hand, the analytical effort to be invested is considerably higher than for the methods that required prior information about the sources (Quass, 2012).

Together with the receptor models, the Lenschow approach has been also used in this work and it is described in detail in Chapter 5.

Concerning the RMs used for ICARUS, PCA is the simplest form of factor analysis. The PCA procedure calculates a new set of independent variables (principal components, eigenvectors) from the original data set of independent variables (chemical species), usually from the covariance matrix. This new set of variables is found as linear combinations of the chemical species so that the observed variations in the system can be reproduced by a smaller number of casual factors (Bari, A. Baumbach, G., 2004). The PMF is described in detail in Chapter 6.

2.2.1 Strengths and limitations of receptor models

In the following lines, the strengths and the limitations of the receptor models are listed (Belis, 2013).Strengths:

- Derive from real-world measurements on one or more sites.
- Appropriate for urban areas and source-oriented sites, but also for regional scale.
- Good output uncertainty estimation.
- Can be used to identify main source categories even when there is poor information about source chemistry and location.
- Mainly used for PM, but also for VOC, PAH and gaseous pollutants.
- Combination with trajectories or wind analysis makes it possible to track the geographic origin of pollution.

Limitations:

- Time series of pollution measurements and chemical characterization are needed.
- Not appropriate for reactive species.
- Provide limited information on secondary inorganic aerosol sources.
- Need for harmonization of methodological steps like estimation of the number and definition of source categories.
- Difficulty to estimate accurately the different sources of carbonaceous fractions due to the limited knowledge of its molecular composition, atmospheric processes and characteristic emission profiles.

One of the complication above listed is the basic assumption that source profiles neither change during air transport nor with time. Therefore, they cannot be applied strictly to secondary aerosol constituents formed in the atmosphere by gas-to-particle conversion processes. As a result, the secondary aerosol constituents tend to be grouped into one source group since they have a common “source”, i.e. formation in air triggered by solar irradiation (Quass, 2012).

In conclusion, the most robust approach to deal with source identification is the use of different models on the same data or on different data of the same area to mutually validate the results and assess the quality of the output quantitatively (Belis, 2013).

2.3 Previous Source Apportionment studies in Europe

Several surveys have been carried out to collect information on the use of models for source apportionment. Viana and co-authors carried out an overview of source apportionment studies in Europe from 1987 to 2007. In their research, PM10 was found to be the preferred target metric (46 %) followed by PM2.5 (33 %) (Viana, M. et al, 2008). However, an increase in the number of studies that target PM2.5 was observed. In 2006 and 2007, 38 % of the new studies found in the literature targeted PM2.5 while only 29 % focused on PM10, thus confirming a change in focus in SA studies in Europe. This focus on the sources of fine aerosols is most probably related to the evidence on the adverse effects of fine particulates on health (Viana, M. et al, 2008).

Regarding the use of different tools for SA, most of the studies applied receptor models (66 %) followed by dispersion models (45 %), as can be seen in Figure 2.3. The need for applying dispersion models for SA can be explained on the basis of the transboundary contributions which represent a significant part of pollutant concentrations in most EU countries, particularly in the case of ozone and particle matter (Fragkou, E. et al, 2012).

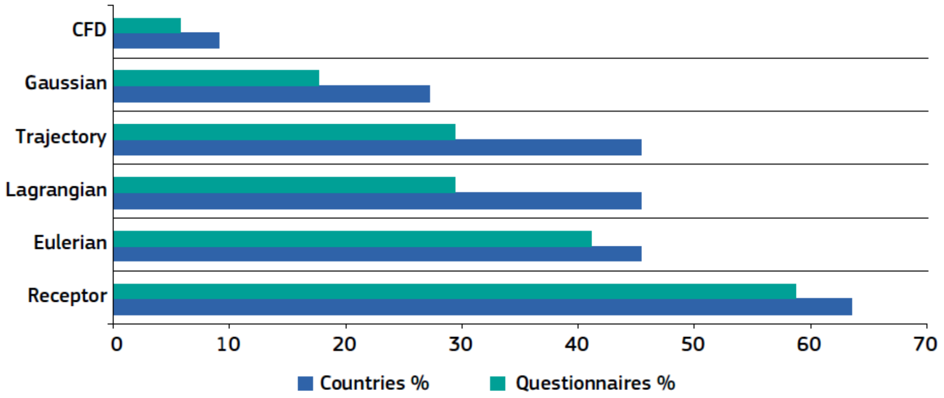


Figure 2.3. Percentage of model type used for SA by different EU countries (Fragkou, E. et al, 2012).

A survey (Karagulian, 2012) on the use of receptor models for particulate matter in Europe between 2001 and 2010, including 79 studies found evidence of a dramatic increase in the number of scientific publications on this topic during the past decade and an increasing number of ready-to-use tools (see Figure 2.4). The highest rate of increase in the number of studies coincides with the entry into force of the limit value for PM10 (1999/30/EC) and the limit value for PM2.5. About 60 % of the studies were carried out in urban background sites, 16 % in source-oriented sites (i.e. traffic measurement station), and 15 % in rural sites.

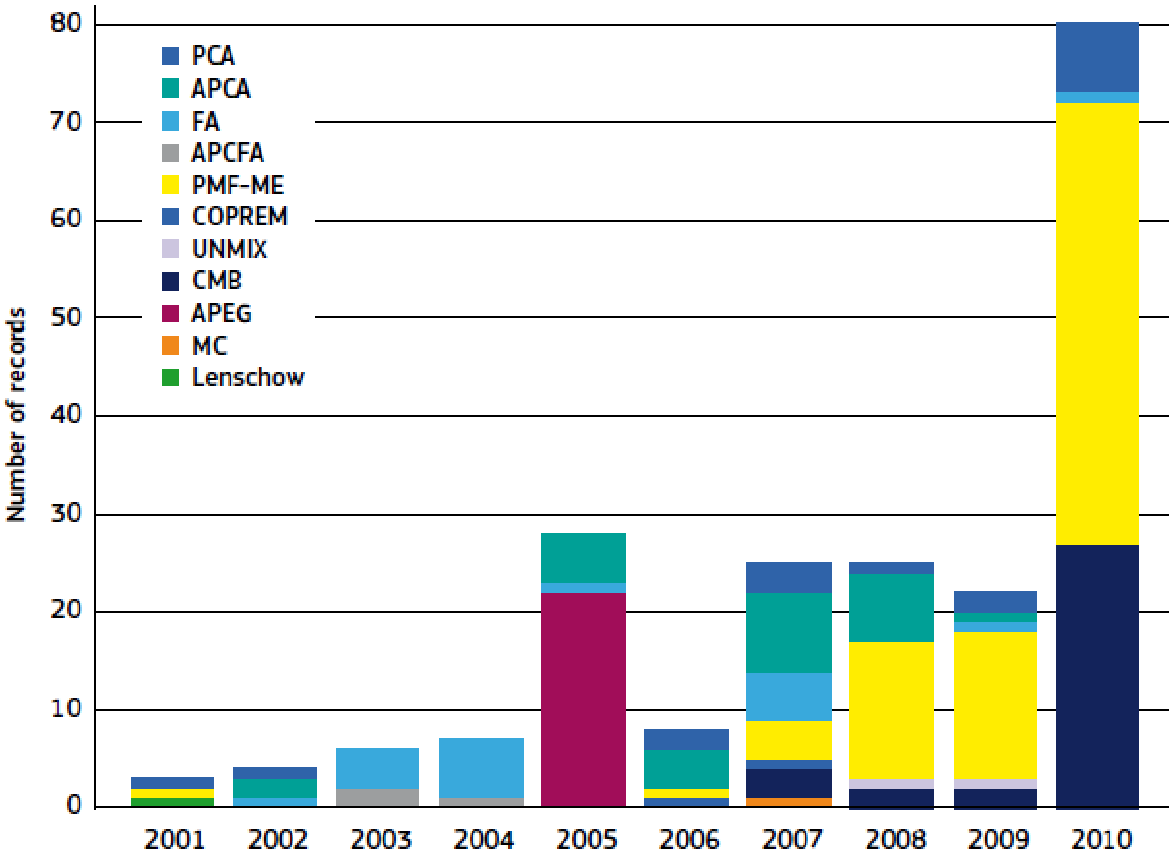


Figure 2.4. Time trend of RM studies in Europe between 2001 and 2010. (Karagulian, 2012)

As can be seen in Figure 2.4, an exponential increase on the use of PMF is observed. This tendency shows that the field of receptor models is developing swiftly with PMF and CMB leading the change. PCA has been also applied recently but in significant less number of studies.

The Lenschow approach has been scarcely used in the last 20 years. It was used once in 2001 (Lenschow, 2001) and in 2007 (Quass, U., 2007). The latter was carried out in Germany and was used to identify the sources of PM10 out in Hessen by using the combination of the Lenschow approach and the PMF. Four years later, a study carried out in Ile-de-France region by applying the Lenschow approach was also implemented for PM10 and PM2.5 (AIRPARIF, 2012). In general, it is worth mentioning that the Lenschow approach has a high uncertainty and should always be combined with a statistical method as the assumptions made by the user could significantly change the results.

3 Methodology

3.1 Sampling campaign

Two sampling campaigns were performed in each participating city for each measurement site during 2017 and 2018. These sites were carefully selected among locations where monitoring stations already existed in order to represent with accuracy the three sampling sites needed: one regional background, one urban background and one traffic site per city. The coordinates of the sampling sites for each city as well as the abbreviation that will be used along this work are listed in Table 3.1. Further information about the sampling campaigns and the characteristics of the measurement stations can be found in the Annex (see Table 11.1).

Table 3.1. Coordinates of the 3 sampling sites in the 6 participating cities.

City	Station	Sampling site	Abbrev.	Coordinates
Athens (NCSRD)	T	Aristotelous	AR	37°59'16"N 23°43'40"E
	UB	Ag. Paraskevi	AGP	37°59'43"N 23°49'09"E
	RB	Aliartos	AL	38°22'31.8"N 23°06'37.0"E
Brno (MU)	T	Svatoplukova	KT	49° 12´ 19.627"N 16° 35´ 49.990" E
	UB	Lány	LA	49° 9´ 54.937"N 16° 34´ 50.925" E
	RB	Košetice (KS)	KS	49° 34´ 24.221"N 15° 4´ 49.002" E
Ljubljana (JSI)	T	MOL – Vosnjakova	MOL	46°03'24.1"N 14°30'10.8"E
	UB	ARSO – Bezigrad	ARSO	46°03'55.6"N 14°30'44.0"E
	RB	TETOL – Zadobrova	TETOL	46°05'37.2"N 14°35'50.3"E
Madrid (ISCIII)	T	E. Aguirre station	ES	40°25'17.63"N 3°40'56.35" W
	UB	Farolillo station	FA	40°23'41.20"N, 3°43'54.60" W
	RB	Casa de Campo station	CA	40°25'09.68"N 3°44'50.44" W
Thessaloniki (AUTH)	T	University campus	UNV	40°37'38.65"N 22°57'34.97" E
	UB	Stavroupoli	STV	40°40'15.82"N 22°56'15.11" E
	RB	Neochorouda	NE	40°44'23.32"N 22°52'33.83" E
Stuttgart (USTUTT)	T	Hohenheimer Straße	HS	48°46'7.23"N 9°11'4.13"E
	UB	Bad Cannstatt	BC	48°48'32.12"N 9°13'47.41"E
	RB	Schwäbische Alb	SA	48°20'44.87"N 9°12'27.35"E

Note: T: Traffic, UB: urban background, RB: regional background

NCSRD: National Center for Scientific Research "Demokritos" MU: Masarykova univerzita JSI: Institut Jozef Stefa ISCIII: Instituto De Salud Carlos III AUTH: Aristotelio Panepistimio Thessalonikis USTUTT: Universität Stuttgart

The PM2.5 samples were collected every 24h by using low volume samplers or automatic sequential samplers. In Stuttgart, particulate samplers MicroPNS type LVS (sequential samplers) were used for the three stations (see Figure 3.1). This microcomputer-controlled air sampler can change up to 16 filters automatically. The sampling specifications are in accordance with EN 12341:2014.

Figure 3.1. Particulate Sampler MicroPNS Type LVS close to a LUBW Station in Hohenheimer Straße (Stuttgart).

The chosen filters were 47 mm TissueQtz (quartz) 25000 QAO-UP PALL membrane filters for low volume samplers (up to 2,3 m^3/h). The methodology used to handle the filters is based on the EN 12341:2014. According to the protocol (ICARUS, Field campaign sampling protocol, 2017), the filters were named with a common filter coding:

“City-Site-Number-Starting sampling date”

As an example, for Stuttgart, in Bad Cannstatt (urban background station):

STU-BC_01-21012018

Blank filters were also taken and coded as follows:

“City-Site_BLK No-sampling period”

As an example for Athens, in Aliartos (regional background station):

ATH-AL_BLK1_10-25012017

3.2 Analysis of the filters

Each filter, after being weighed following the European standard EN 12341:2014, was appropriate divided into three pieces using surgical scalpel (see Figure 3.2) in order to be analysed for all the proposed species as follows:

- A quarter (1/4) of the filter was used for OC/EC analysis,
- another quarter (1/4) for ions,
- and half filter for metals (using XRF – non-destructive method) and then for PAHs.

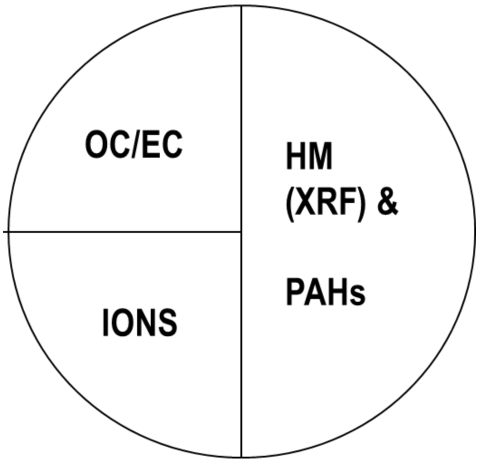


Figure 3.2. Division of the filter for chemical analysis.

Five different groups of chemical species were analysed, namely anions, cations, metals, OC/EC and PAHs. The methodology and the species are listed in Table 3.2.

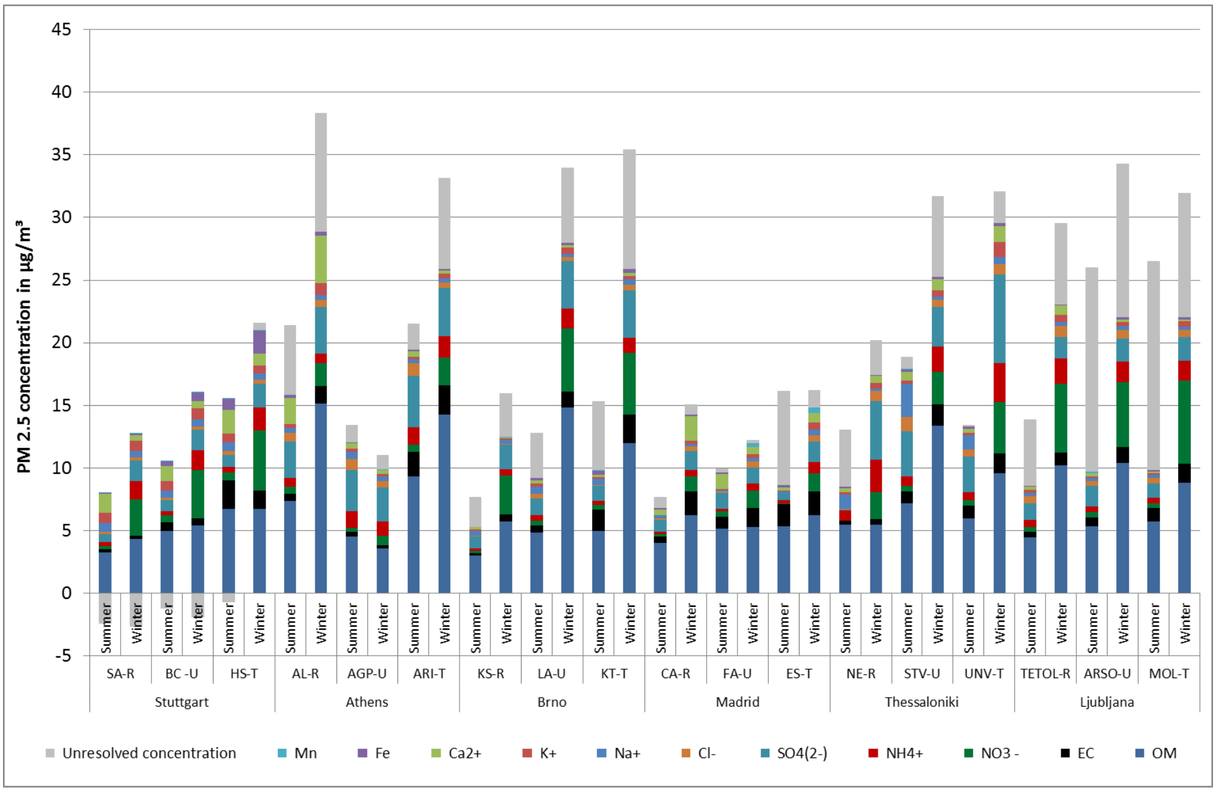
The calculation of the uncertainties has followed the guideline ISO 20988:2007 for estimating measurement uncertainty in air quality measurements.

Table 3.2. Norms and analyzed species of the PM2.5 fraction.

	Norm	**Analysed by**	**Species**
Cations	DIN CEN/TR 16269:2011	AUTH ISCIII	NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}
Anions	DIN CEN/TR 16269:2011	AUTH ISCIII	Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}
Metals	VDI 2267 Blatt 12:2008	NCSRD ISCIII	Na, Co, Mg, Ni, Al, Cu, Si, Zn, S, As, Cl, Cd, K, Br, Ca, Sr, Ti, Sn, V, Sb, Cr, Ba,Mn, Hg, Fe, Pb
Carbon	EN 16909:2017	ISCIII	OC, EC
PAHs	ISO 16362:2005	NSCR MU AUTH ISCIII	Naphthalene, 2-methylnaphthalene 1-methylnaphthalene, Acenaphthylene 1,2-dimethylnaphthalene, 2,6-dimethylnaphthalene Acenaphthene, 2,3,5-trimethylnaphthalene Fluorene, dibenzothiophene Phenanthrene, 2-methylphenanthrene 1-methylphenthrene, 3,6-dimethylphenanthrene Anthanthrene, Fluoranthene Pyrene, benz(a)anthracene, chrysene Benzo(b)fluoranthene, Benzo(k)fluoranthene Benzo(e)pyrene, Benzo(a)pyrene, Perylene Indeno(123-cd)pyrene, Dibenzo(ah)anthracene Benzo(ghi)perylene, Benzo-Naphtho-Thiophene Coronene, Fluorene, Benzo(ghi)fluoranthene Cyclopenta(cd)pyrene, Triphenylene Benzo(j)fluoranthene, Dibenzo(ac)anthracene Chrysene, Retene, Benzo(a)anthracene Benzo(b)fluorene

4 General overview of the results for the six participating cities

In Figure 4.1, the average concentration in µg/m³ of the major species for each site/city during the winter and the summer campaigns are presented.



Note: T:Traffic, U:urban, R:regional

Figure 4.1. PM2.5 concentration measured in the participating cities during the summer and winter campaign.

The principal aspects to consider from Figure 4.1 are listed below.

- As expected, the average concentration of PM2.5 measured in each site during the winter campaign was higher than the concentration of PM2.5 measured during the summer campaign as surface inversions are more common in winter, hindering the dilution of the air pollution and causing higher concentrations of air pollutants in the ambient air. Only one exception can be seen, the urban site (AGP) in Athens. However, it should be noticed that the weather conditions during the measurement campaign together with the uncertainty of the gravimetric analysis are needed for further conclusions.

- The regional site of **Athens** in winter presents the highest average concentrations of PM2.5, with an amount of organic matter (OM) twice the average concentrations of OM in the other cities. The reason can be likely found in the biomass burning (domestic as well as agricultural) occurring nearby the measurement station during the cold period. It should also be considered the contraction of a road nearby the monitoring station as a possible aggravating factor.

- The urban (ARSO) and traffic (MOL) sites in **Ljubljana** present very high values of $PM_{2.5}$ during both campaigns which indicates a high probability of an average yearly value of $PM_{2.5}$ exceeding the limit value (25 µg / m^3).

- **Stuttgart** presents negative unresolved concentration for most of the sites and periods which indicates that the measured mass in the filter was smaller than the sum of the analysed species. The reason for that is due to problems in the process of weighing the filters.

- Regarding the regional site (CA) in **Madrid**, the concentration of PM2.5 in winter presents the same average concentration than in the traffic site and higher than in the urban background station. It is also worth mentioning that the organic matter concentration during the measurement campaigns remains steady during both campaign in the three sites.

- The **city of Brno** presents extremely high peaks during winter in the urban (LA) and traffic (KT) site. It doubles the amount of organic matter, probably due to the use of biomass in households for heating purposes together with the temperature inversion phenomena.

- **Thessaloniki** also shows high concentration of PM2.5 in the urban (STV) and traffic (UNV) sites in winter, due to mainly organic carbon.

5 Lenschow approach

5.1 Fundamentals about the Lenschow approach

The Lenschow approach is based on the Spatial Incremental Approach, the most widely and simple method of source apportionment. Using the Spatial Incremental approach, a simple source apportionment analysis is carried out (see Figure 5.1) by considering the scenario of an urban background as an island of elevated PM-levels arising from a regional background, and on top definite peak concentrations due to traffic hotspots at kerbside locations. Hence, by calculation of the spatial increments (e.g. traffic - urban background, urban background - regional background) basic assessments of the shares of emissions from the different "source areas" can be obtained (Lenschow, 2001). Consequently, for this method the measurements have to be simultaneously taken in three locations: regional background, urban background and a traffic hotspot (Hopke, 1991).

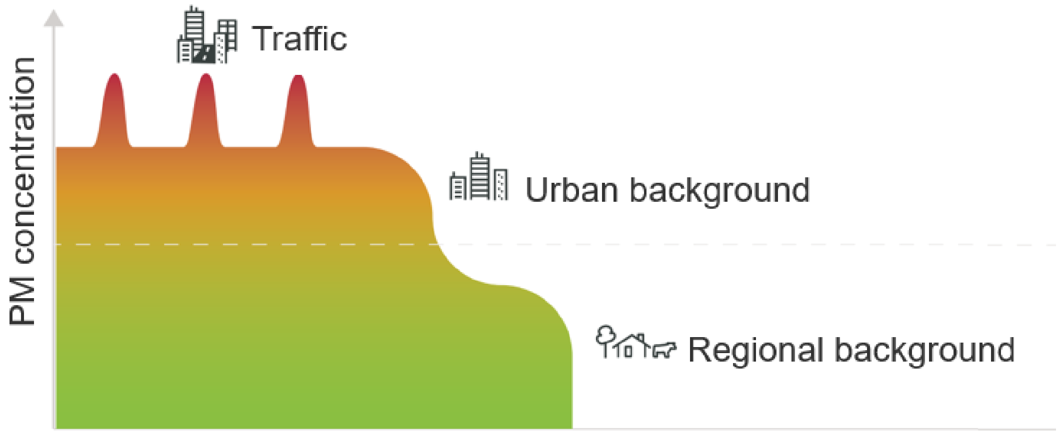


Figure 5.1. Schematic profile of the ambient PM concentration according to the Spatial Incremental approach. Adapted from (Lenschow, 2001)

With the objective of assessing the full impact of a given city, the following assumptions need to be fulfilled (Lenschow, 2001); (Thunis, 2018).

- Concentrations measured at only one carefully selected station per type (traffic, urban and regional background) can be taken as representative for the other stations.
- The differences of particulate matter and its chemical components between the traffic station and the urban background station can be attributed to the local influence of traffic on the adjacent street.

- The differences of particulate matter and its chemical components between the urban background station and the regional background station can be attributed to the sources of agglomeration.
- The urban impact at the regional background site is negligible.

The Lenschow approach goes a step further including the chemical composition for the major compounds as well as emission inventories for the corresponding areas. Having both of them, the apportionment is done according to the relative shares of the corresponding emissions for each environment (Hopke, 1991). The main advantage of this strategy is the simplicity of the method and the consequent low mathematical treatment required for the data processing.

The validity of the results depends on the accuracy and completeness of the emission registers (Hopke, 1991). For some source types, the distribution depends on assumptions made that may have a high degree of uncertainty (Quass, 2012).

5.2 Analysis of the input data and further considerations

The evaluation has been carried out for the six participating cities (Athens, Brno, Ljubljana, Madrid, Thessaloniki and Stuttgart) in three sampling sites (traffic, urban background and regional background) for the two measurement campaigns, winter and summer (see Table 3.1).

The filters for PM2.5 used during the measurements were divided into three pieces according to the protocol in order to perform the chemical analysis for different species in different institutes. Five different groups of chemical species were analysed, namely anions, cations, metals, OC/EC and PAHs. The last group has not been used for this method as the concentrations are in the order of ng / m^3 and the Lenschow approach only considers major species (in µg / m^3). The chemical composition used for the Lenschow approach is shown in Table 5.1.

Table 5.1. Analysed composition of the $PM_{2.5}$ samples used in the Lenschow approach.

Cations	Anions	Metals		Carbon
NH_4^+	Cl^-	Na	Co	Organic carbon (OC)
Na^+	NO_3^-	Mg	Ni	Elemental Carbon (EC)
Mg^{2+}	PO_4^{3-}	Al	Cu	
K^+	SO_4^{2-}	Si	Zn	
Ca^{2+}		S	As	
		Cl	Cd	
		K	Br	
		Ca	Sr	
		Ti	Sn	

With the idea of having an overview of the main species that characterize the air in each city, only the key components that have been analysed are shown in the graphs. Those components represent at least 96 % of the measured mass. Other methods like PMF or PCA should be used to evaluate trace elements (Quass, U., 2007).

To avoid double counting, chloride (Cl^-), water-soluble potassium (K^+), sodium (Na^+), calcium (Ca^{2+}) and sulphate (SO_4^{2-}) have been included in the sum while total sulphur (S), chlorine (Cl), sodium (Na), potassium (K) and calcium (Ca) have been excluded (Huang, 2014). Concentration data below the detection limit has been neglected. Other species with low number of available data have been excluded, as well. The organic carbon has been replaced by the organic matter (OM) by using a factor of 1.4 (Quass, U., 2007) (Tomasi, 2016). OM to OC ratios reported in the literature range between 1.2 for fresh organic aerosols and 2.4 for highly processed ones (Aiken, 2008).

Negative values after the subtraction of urban concentrations from traffic concentrations and regional data from urban data have been neglected. Moreover, days in which the samples have not been taken in the three sites but only in one or two sites have been discarded. This has caused a reduction of the available data which in some cases like in the city of Athens has invalidated the results as the available data for the Lenschow approach was not enough to be representative for the whole campaign.

National emission inventories for the five countries (Greece, Czech Republic, Slovenia, Spain and Germany) reported under the CLRTAP (Convention on Long-Range, Transboundary Air

Pollution) have been applied for the source apportionment of the regional background. Emission inventories for the corresponding cities have been used for the source apportionment in urban areas. The required data have been the emissions of SO_2, NO_x, NH_3, NMVOC, POC (primary organic carbon) and black carbon (BC) (see Figure 5.2). The results have been compared with the PM2.5 emission data from the emission inventories.

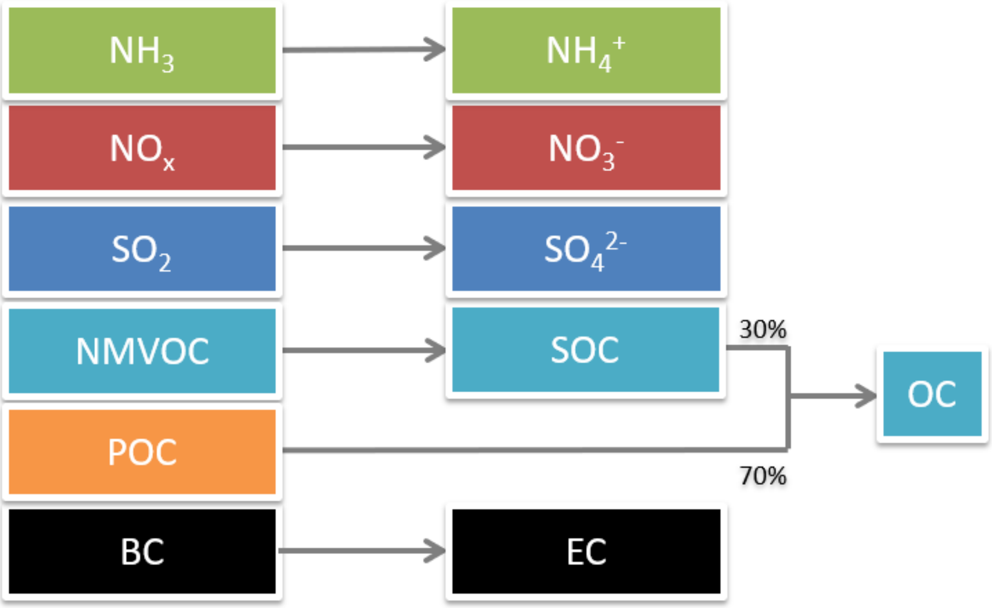


Figure 5.2. Scheme to couple the chemical profiles and the emission inventories.

As shown in Figure 5.2, it has been assumed that the emissions of the SO_2, NO_2, NH_3 and BC are the sources of SO_4^{2-}, NO_3^-, NH_4^+ and EC, respectively. It should be stressed that EC is not equivalent to black carbon (BC), which is defined and measured based on optical properties and absorbs light more strongly than EC. However, a significant fraction of the EC is BC. Hence, the contribution of the sources of BC have been assumed to be the same as for EC, which is a primary pollutant emitted directly from combustion sources (Shakya, Ziemba, & Griffin, 2010).

Different assumptions can be stated for the calculation of the source contribution to the organic carbon fraction. OC has two different sources, namely primary organic carbon (POC) if it is emitted directly and secondary organic carbon (SOC) if it is formed from the partitioning to the condensed phase of semi- or non-volatile products of the oxidation of volatile organic compounds or by aqueous-phase processing. POC and SOC are generated from both anthropogenic and biogenic sources (Shakya, Ziemba, & Griffin, 2010).

For the regional background, the SOC have been assumed to come exclusively from the NMVOC. The sources and its contribution on the NMVOC concentration can be found in the national emission inventories. Hence, the natural sources of NMVOC are not considered. The source contribution of POC for the participating countries has been provided by the department of Technology Assessment and Environment of the Stuttgart University.

Having the source contributions of POC and SOC, the OC has been calculated knowing that it is usually formed by 80 % of the SOC and 20 % of POC (Tsimpidi, Vlassis, Spyros N., & Lelieveld, 2016).

Regarding the urban area, no black carbon data has been reported in the emission inventories of the cities, except from the city of Madrid as it is not mandatory for it to be included. Thus, five sources have been assumed to be the main sources of emissions at the urban site (Lenschow, 2001), namely: industry (7 %), traffic (70 %), waste treatment and disposal (9 %), use of solvents (7 %) and households (7 %). The percentage has been combined with the national OC/BC ratio for each city to know the percentage of organic matter per category.

At the hotspot measurement station mainly traffic has been taking into account to be the source of OM and EC (Quass, U., 2007). The 80 % of all the OM, EC, NO_3^- and NH_4^+ has been assumed to come from the exhaust pipes whereas the 20 % left contribute to the tyre and brake wear and the resuspension of particles, according to the literature (Quass, U., 2007). The metal components (mainly Fe and Ca) and 70 % of the unidentified material, belong also to this category. The SO_4^{2-} has been divided into industry (80 %) and households (20 %).

Natural sources have been estimated for the three sites as the sum of ions (Na^+, Cl^-). As Calcium could have either natural origin or anthropogenic origin (road dust), it has been divided 50/50. Finally, the unidentified material has been categorized as unknown sources for all the sites (100 % in regional and urban sites and 30 % in traffic).

To enable the presentation of sectoral emission trends, individual NFR (Nomenclature for Reporting) sources categories for the European Emission Inventories have been aggregated into nine groups: seven groups representing the anthropogenic emissions involving all the individual NFR source categories (see Table 11.2 in the Annex), natural sources and unknown sources

5.3 Lenschow Approach Results

5.3.1 Results for Athens

Due to the high concentration of PM2.5 measured in the regional background during summer and winter the Lenschow approach cannot be applied in the city of Athens as the difference in the PM2.5 concentration between the urban and the regional background would give negative results in the urban site. In the following charts, the average composition per site is discussed for the two campaigns.

5.3.2a Summer campaign results for Athens

The chemical composition per site in the city of Athens during the summer campaign is shown in Figure 5.3.

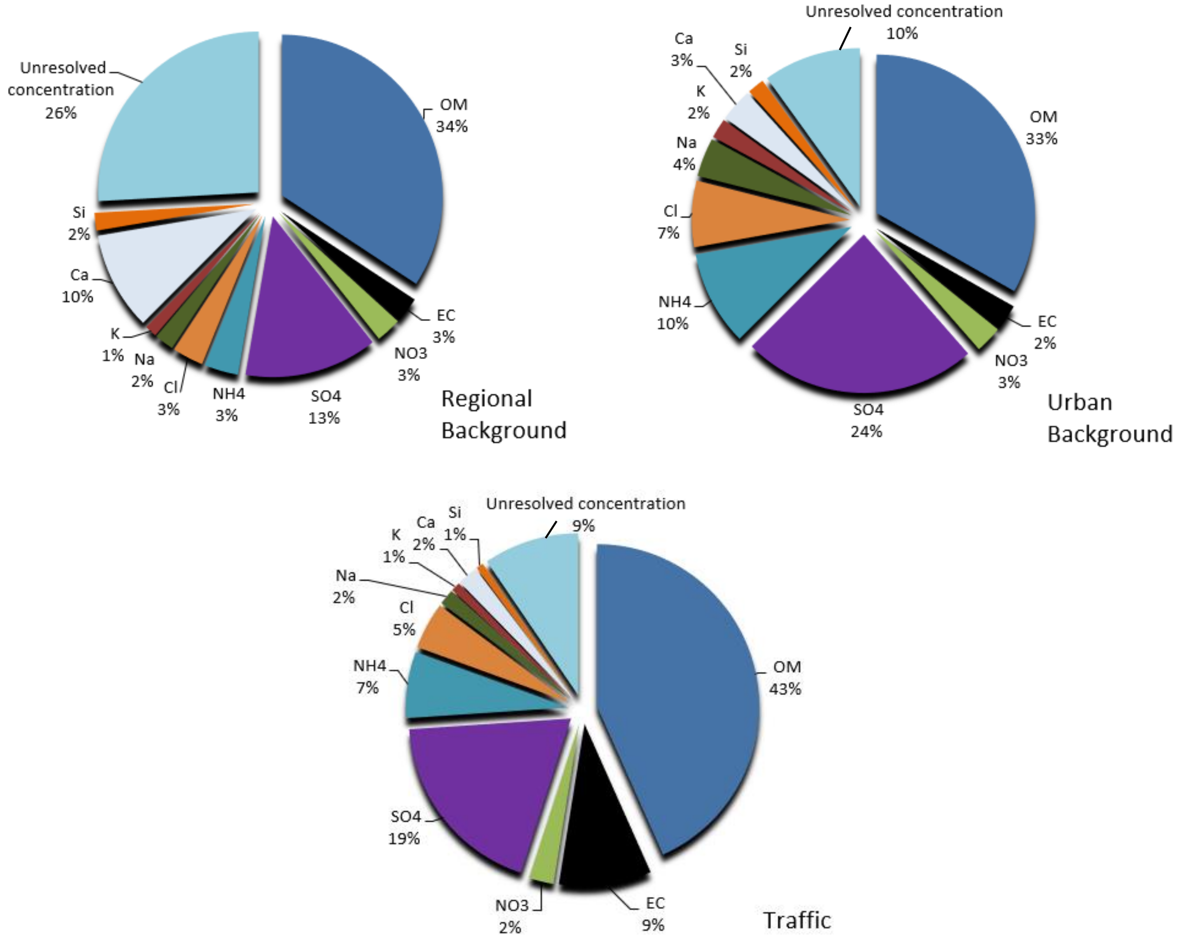


Figure 5.3. Chemical composition of PM2.5 per site in Athens during the summer campaign.

As can be seen in Figure 5.3, elemental carbon has a significant contribution in the traffic site. Together with the organic matter constitute more than 50 % of the concentration of PM2.5. Sea sprays (Cl^- , Na^+) seem to have more impact in the traffic and urban sites (7 % and 11 %, respectively) than in the regional background (5 %) as they are closer to the Mediterranean Sea.

The average PM2.5 concentration was 19.9 µg/m^3 in the regional site (Aliartos), 11.9 µg/m^3 in the urban background site (Aliartos) and 19.6 µg/m^3 in the traffic site (Aristotelus). The regional site presents higher PM2.5 concentrations than the urban background, mainly due to the high contribution of the unresolved material. Moreover, only during 14 days (from 30.5.17 to 12.06.17) parallel measurements were carried out in the traffic and urban stations, as it is shown in Figure 5.4.

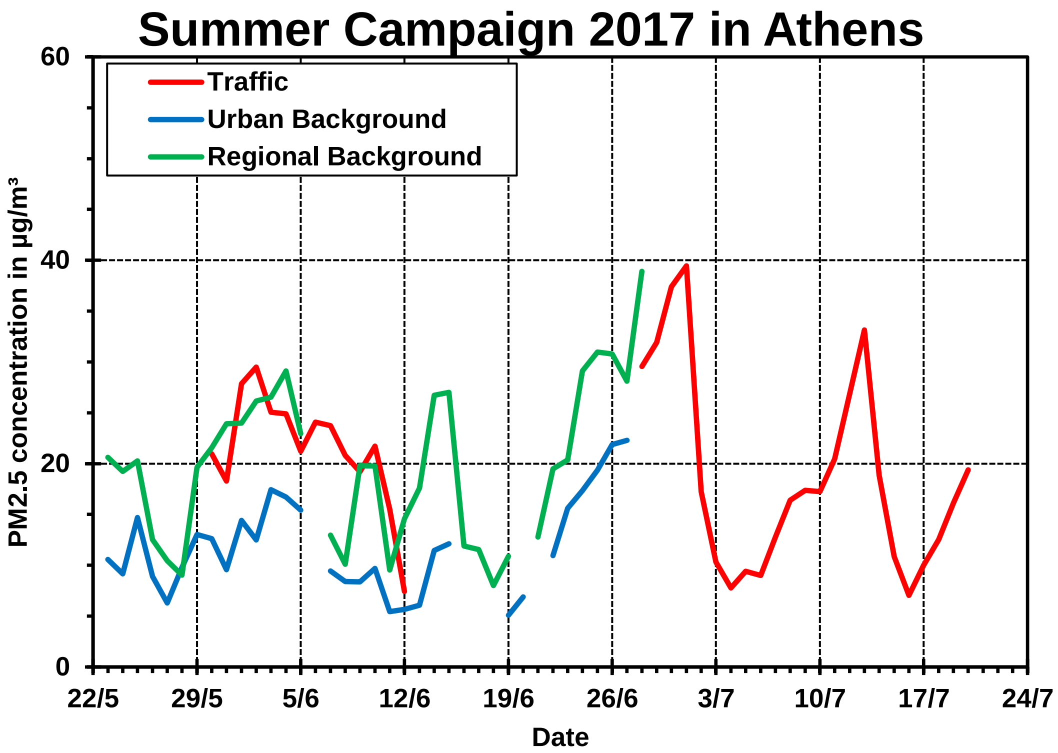
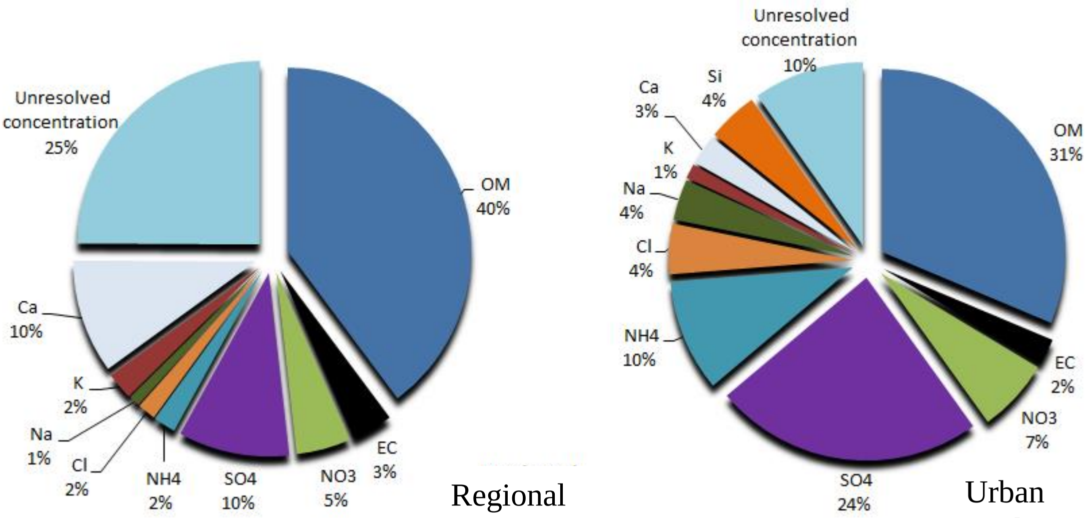


Figure 5.4. Daily evolution of PM2.5 concentrations for the three sampling sites in Athens during the summer campaign.

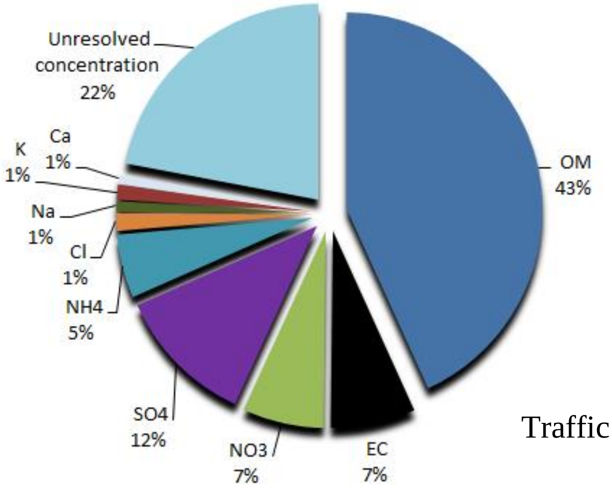
5.3.2b Athens winter campaign

The chemical composition per site in the city of Athens during the summer campaign is shown in Figure 5.5.



Regional Background

Urban Background



Traffic site

Figure 5.5. Chemical composition of PM2.5 per site in Athens during the winter campaign.

The pie charts from Figure 5.5 show a similar component contribution to the sector diagrams shown in Figure 5.4 for the summer campaign. Elemental carbon and organic matter represent the 50 % of the PM2.5 concentration. An increase in the share of NO_3^- to the total PM2.5 concentration can be seen. The reasons for that are favourable conditions for NO_3^- formation during the cold season as low temperature and stable meteorology favour the reaction of ammonia with nitric acid to form ammonium and nitrate (Khan, 2009).

The average PM2.5 concentration was 38,0 µg /m³ in the regional site (Aliartos), 10,8 µg/m³ in the urban site (Aliartos) and 29,6 µg/m³ in the traffic site (Aristotelus). The daily concentration of PM2.5 during the winter campaign is shown in Figure 5.6.

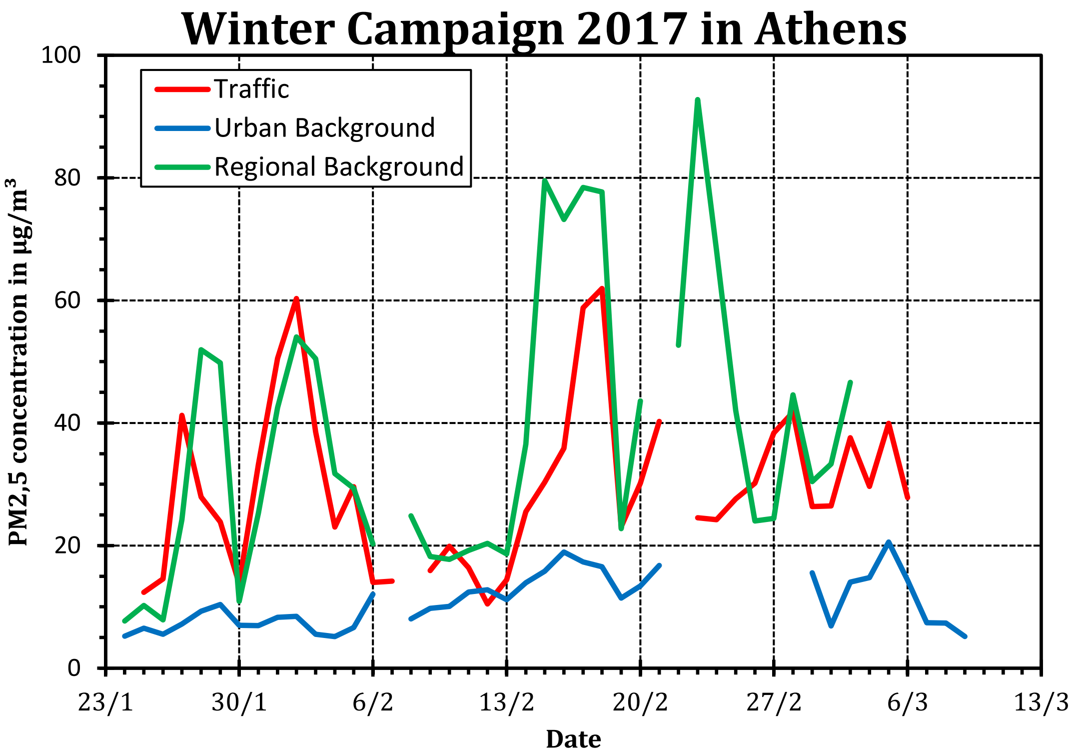


Figure 5.6. Daily evolution of PM2.5 concentrations for the three sampling sites during the winter campaign.

As can be seen from Figure 5.6, daily measurements of PM2.5 in the regional background are most of the days equal or bigger than the PM2.5 concentration at the traffic site. This fact invalidates the site to be taken as a representative for the regional background. Moreover, PM2.5 concentrations measured in the urban station range from a few micrograms per cubic meter to 20 µg/m³, which is the interval that characterize the regional background.

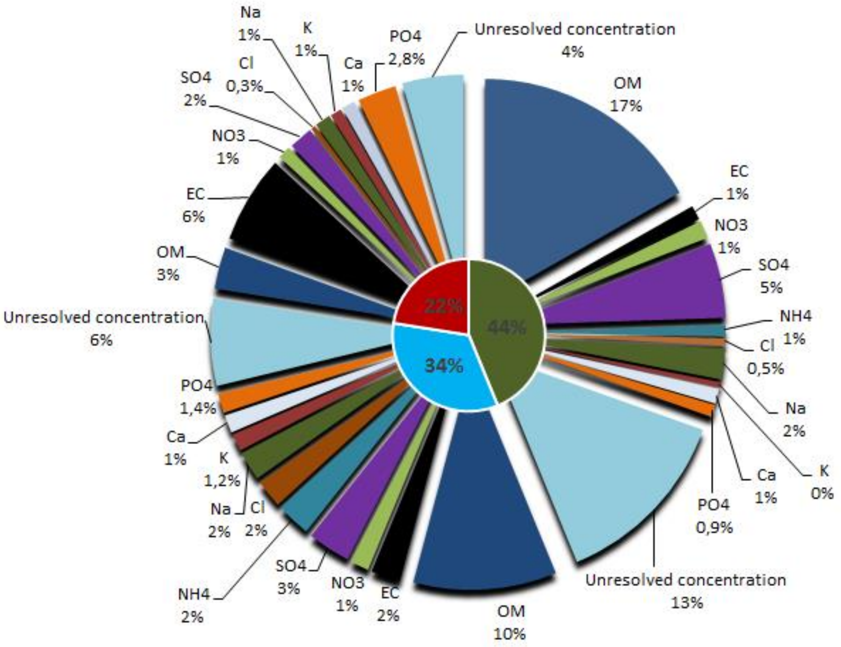
After a geographical analysis and the evaluation of the PM2.5 data, it can be concluded that the regional station does not fulfil the characteristics to be used as a regional background station. Furthermore, traces of elements like Fe, Mn and Pb were found in higher concentration in the regional background station than in the urban background and traffic stations during both campaigns.

5.3.2 Results for Brno

The following paragraphs contain the chemical composition of the measured PM2.5 concentration for the summer and winter campaigns as well as the source apportionment calculated with the Lenschow approach for the city of Brno.

5.3.3a Summer campaign results for Brno

In Figure 5.7 the chemical contribution of the main species in each area is presented for the city of Brno during the summer campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.7. Percentage of species contributing to the PM2.5 per source area in Brno during the summer campaign

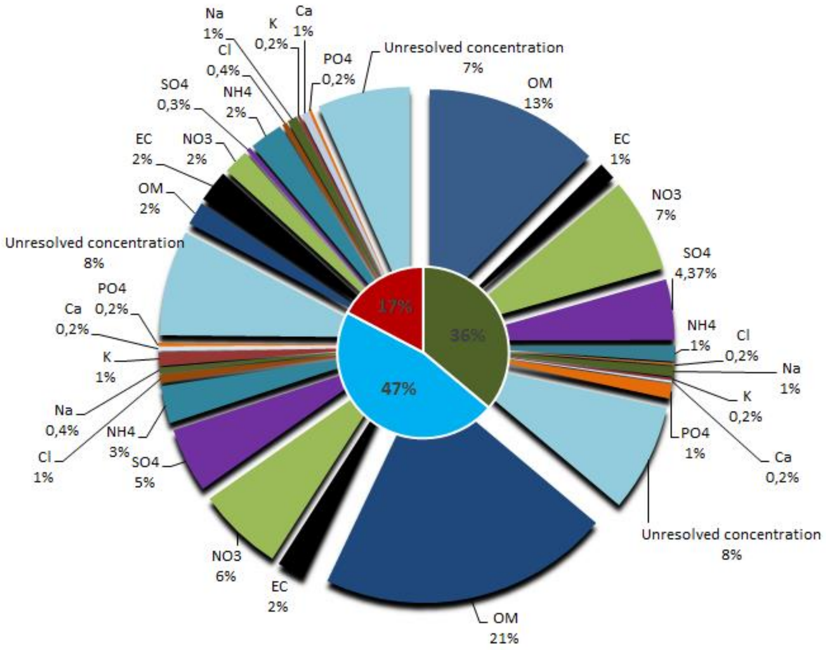
As it is shown in Figure 5.7, the 44 % of the total emission share corresponds to the regional background which is attributable to organic matter from anthropogenic or natural sources and inorganic aerosols originating from Europe-wide gaseous emissions.

During the summer the urban contribution represents 34 % of the total share of emissions. The chemical composition is very similar to the regional background, but with an increase in the percentage of elemental carbon and a decrease in the contribution of organic matter.

The traffic contributes with the 22 % of the total share of emissions and it is mainly characterized for the high concentration of elemental carbon, meaning that a minimum of 27 % of the emissions caused by traffic are coming from the exhaust pipe of the cars, as elemental carbon is exclusively a by-product of incomplete combustion.

5.3.3b Winter campaign results for Brno

In Figure 5.8, the chemical contribution of the main species in each area is presented for the city of Brno during the winter campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

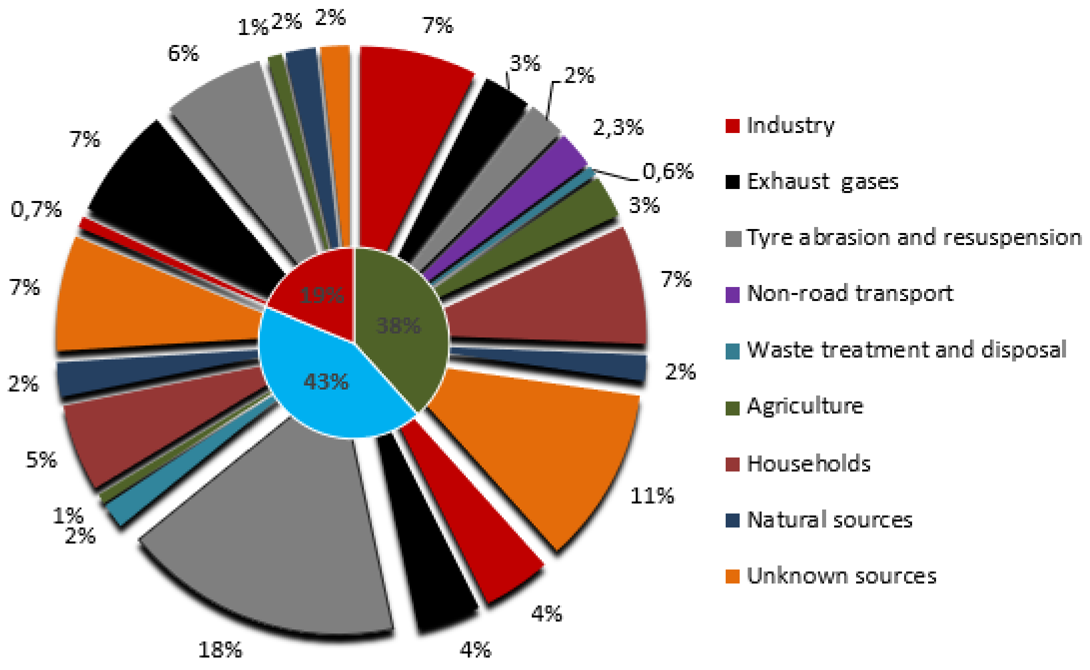
Figure 5.8. Percentage of species contributing to the PM2.5 per source area in Brno during the winter campaign.

As it is shown in Figure 5.8, the 36 % of the total emission share corresponds to the regional background which is again attributable to organic matter from anthropogenic or natural sources and inorganic aerosols originating from Europe-wide gaseous emissions. It can be highlighted the increase of the NO_3^- contribution which is higher than in summer (from 1 % in summer to 7 % in winter). This is due to the favourable conditions for NO_3^- formation during the cold season as low temperature and stable meteorology favour the reaction of ammonia to form nitrate (Khan, 2009).

During the winter, the urban contribution represents 47 % of the emission source mainly caused by the increase of organic matter which could be related with biomass combustion. The traffic represents 17 % of the emission source.

5.3.3c Lenschow approach results for Brno

To evaluate the emission sources in Brno, the average of the two campaigns for the chemical data has been calculated. The emission inventory data has been obtained from the "Czech informative inventory report 2018 - Submission under the UNECE Convention on Long-range Transboundary Air Pollution (2018)" Emission sources for the urban area have been reported within the ICARUS Project "D2.2 Report and data on emission inventory at city level for the considered pollutants and GHGs for the years 2015, 2020 and 2030" (Neuhäuser, 2017). The results of the source apportionment obtained through the application of the Lenschow approach are reported in Figure 5.9 and Figure 5.10.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.9. Lenschow approach for the source apportionment of PM 2.5 in the three areas in Brno.

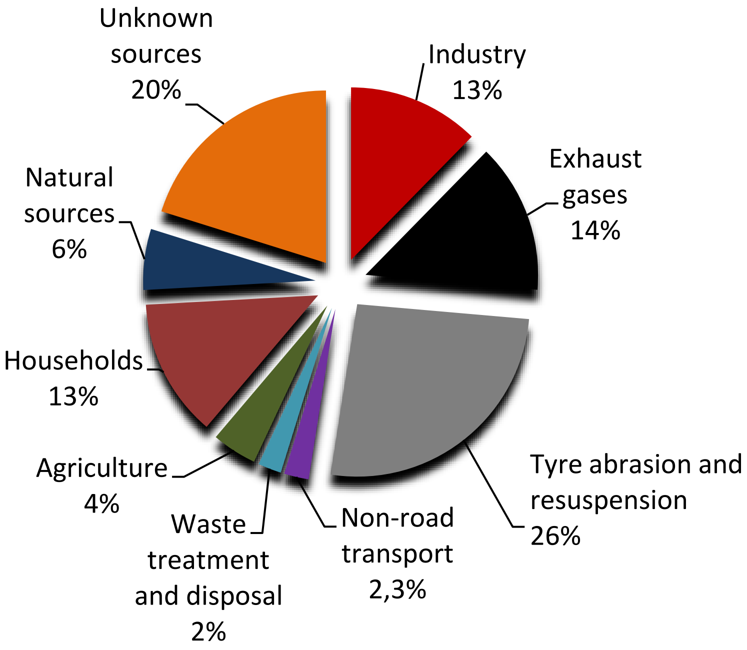


Figure 5.10. Source apportionment in Brno per emission source.

As can be seen in Figure 5.9, the 38 % of the emission sources have a rural origin. Out of them, a minimum of 7 % comes from the residential sector and 7 % from the industry and energy production. This share could be even bigger as 11 % of the emission sources in the regional background have not been classified.

In the urban background, which accounts for 43 % of the total emission source, is worthy to mention the relevant role of the traffic (22 %), mainly due to particle resuspension and abrasion of tyres and brakes (18 %) and exhaust sources (4 %).

The traffic area represents 19 % of the emission source. The main contributors are exhaust sources (7 %) and tyre abrasion and resuspension (6 %).

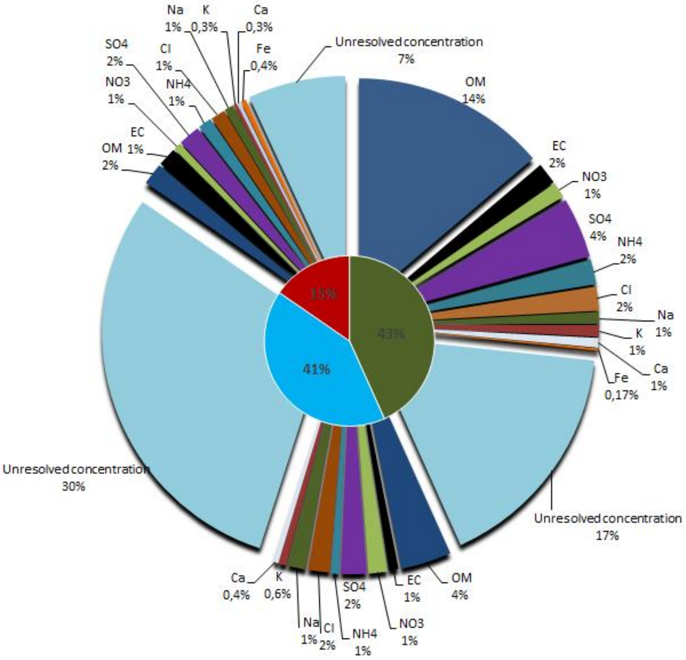
In general, 40 % of the emissions are due to road transport. Road abrasion and resuspension plays a significant role, following by households and industry. On the other side, it can be seen in Figure 5.10 that the non-road transport (caused by aviation, railways and navigation), waste treatment and disposal and agriculture have a small contribution, less than 5 % each.

5.3.3 Results for Ljubljana

The following paragraphs contain the chemical distribution of $PM_{2.5}$ concentration for the summer and winter campaigns as well as the source apportionment calculated with the Lenschow approach for the city of Ljubljana.

5.3.4a Summer campaign results for Ljubljana

In Figure 5.11 the chemical contribution of the main species in each area is presented for the city of Ljubljana during the summer campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.11. Percentage of species contributing to the PM2.5 per source area in Ljubljana during the summer campaign.

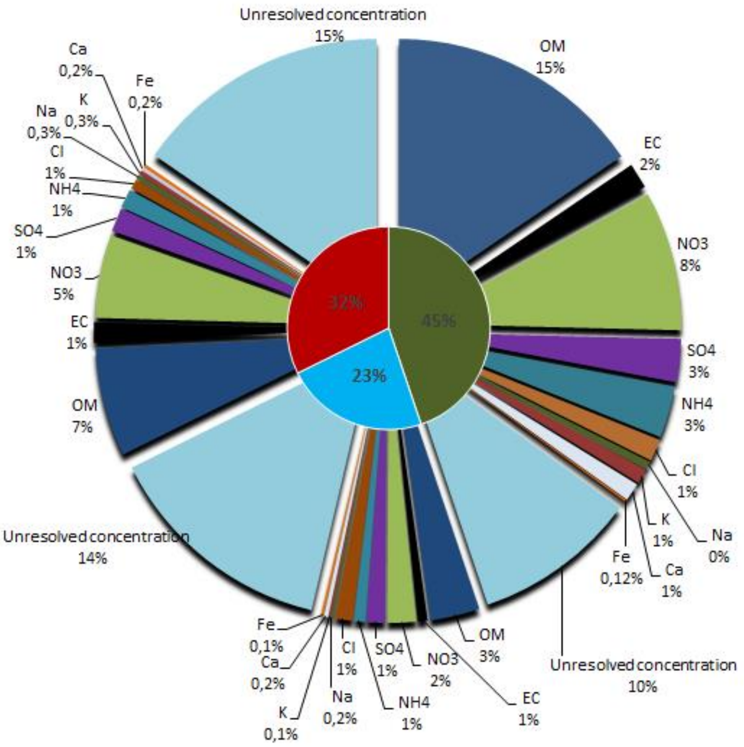
As can be seen in Figure 5.11, regional background represents the 43 % of the emission sources mainly composed by secondary aerosols (nitrate, sulphate, ammonia and chloride ions). The organic matter, together with potassium traces, is associated with biomass combustion.

The urban source accounts for the 41 % of the total share. The significant amount of unresolved concentration should be highlighted (30 %). The rest of the sector is formed by organic matter (4 %), elemental carbon (1 %) and secondary aerosols.

Traffic shows a contribution of 15 %. This sector reveals some Fe traces (0,4 %), that are characteristic for non-exhaust traffic emissions.

5.3.4b Winter campaign results for Ljubljana

In Figure 5.12, the chemical contribution of the main species in each area is presented for the city of Ljubljana during the winter campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.12. Percentage of species contributing to the PM2.5 per source area in Ljubljana during the winter campaign.

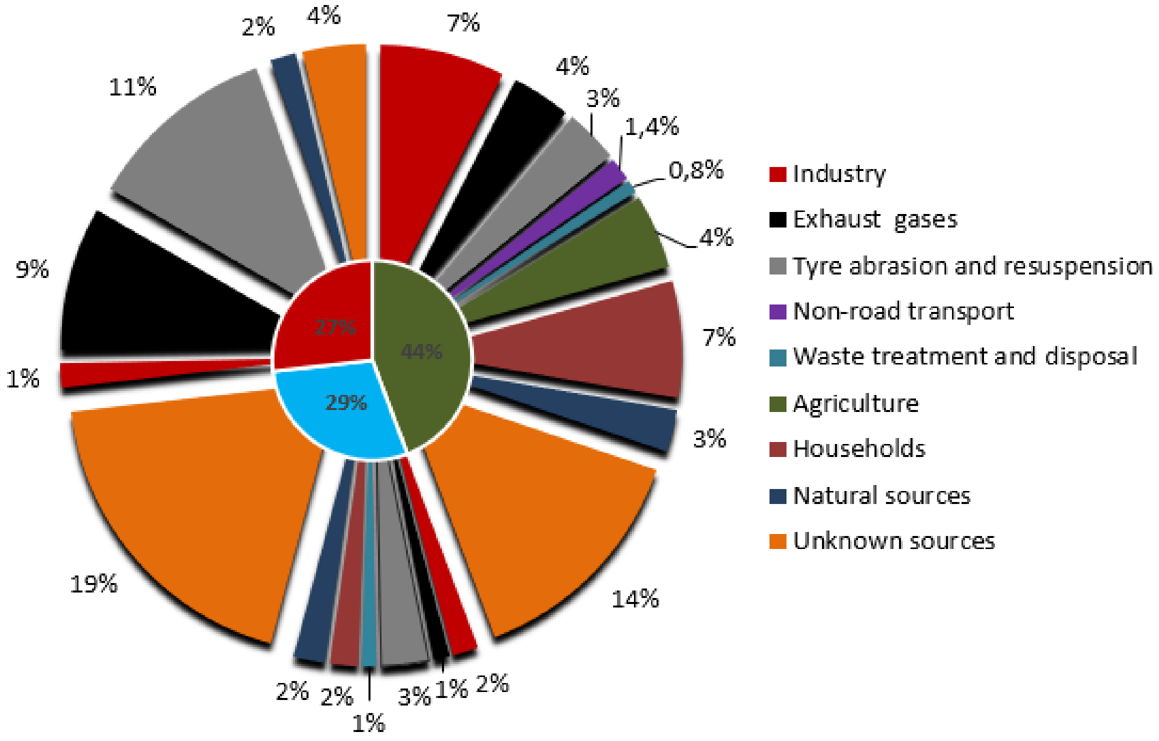
As can be seen in Figure 5.12, the 45 % of the total emission share corresponds to the regional background which is mainly attributable to organic matter from anthropogenic or natural sources and secondary aerosols. Similarly to Brno, the amount of nitrate considerably increases during the cold period.

Urban sources represent the 23 % of the total and it is characterized by a high amount of unidentified material (14 %).

Traffic accounts for the 32 % of the total emission sources. It should be highlighted the substantial amount of nitrate found in this source area. Moreover, traces of Fe and Ca, that are associated with road dust and non-exhaust traffic emissions, are also found in a significant amount (0,2 % each component).

5.3.4c Lenschow approach results for Ljubljana

In order to evaluate the emission sources in Ljubljana, the average of the two campaigns for the chemical data has been calculated. The emission inventory data has been obtained from the “Slovenia’s Informative Inventory Report 2018. Submission under the UNECE Convention on Long-range Transboundary Air Pollution (2018)”. Emission sources for the urban area have been reported within the ICARUS Project “D2.2 Report and data on emission inventory at city level for the considered pollutants and GHGs for the years 2015, 2020 and 2030” (Neuhäuser, 2017). The results of the source apportionment obtained through the application of the Lenschow approach are reported in Figure 5.13, Figure 5.14 and Figure 5.15.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.13. Lenschow approach for the source apportionment of PM2.5 in the three areas in Ljubljana.

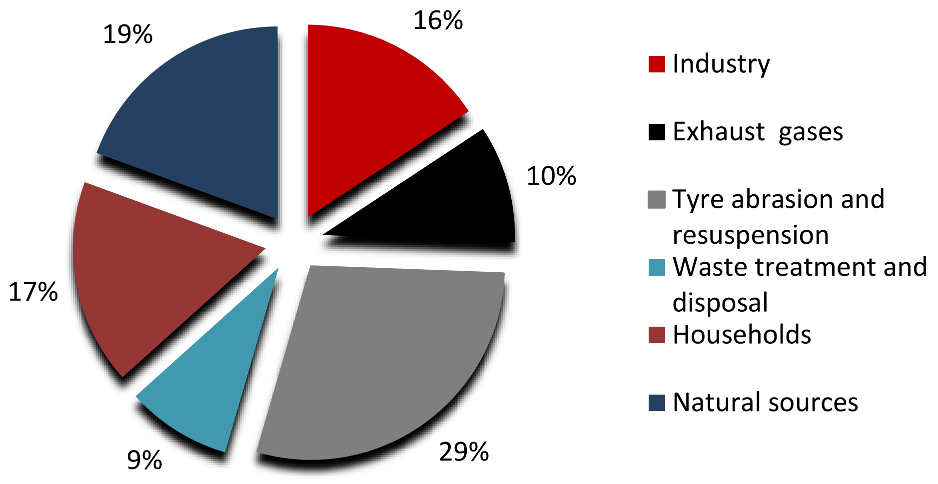


Figure 5.14. Zoom of the source apportionment of PM2.5 in the urban area in Ljubljana.

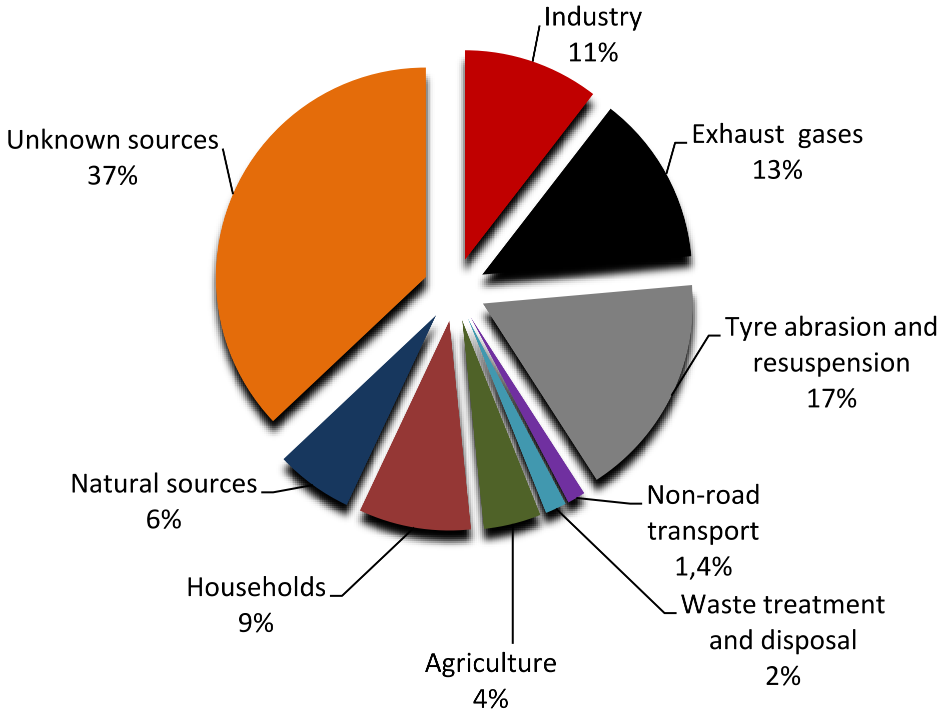


Figure 5.15. Source apportionment in Ljubljana per emission source.

As reported in Figure 5.13, the regional background in Ljubljana represents the 44 % of the emission sources. It should be highlighted that the major contribution comes from households (7 %). As the amount of unidentified material during the analysis was very high, the urban sources without counting the unknown sources as been depicted in Figure 5.14 to better visualize the shares.

Similarly to Brno, traffic emissions have a big proportion of the total share of emissions in urban areas. Exhaust sources are the source of 10 % of the analysed pollutants whereas 30 % come from the tyre abrasion and resuspension of particles.

As reported in Figure 5.15, the amount of unknown sources is significantly high (37 %). This is due to the big difference between the sum of the chemical components and the weighed mass of the filters. Some of the possible reasons could be (Belis et al, 2014) the following:

a) not all the relevant chemical components have been determined;
b) the mass measurement includes water adsorbed to particles that is not quantified in the chemical analyses,
c) the selected coefficient for converting OC to OM is not optimal for the study area;
d) the elements that have been assumed to be present as oxides and carbonate have not been taken into consideration.

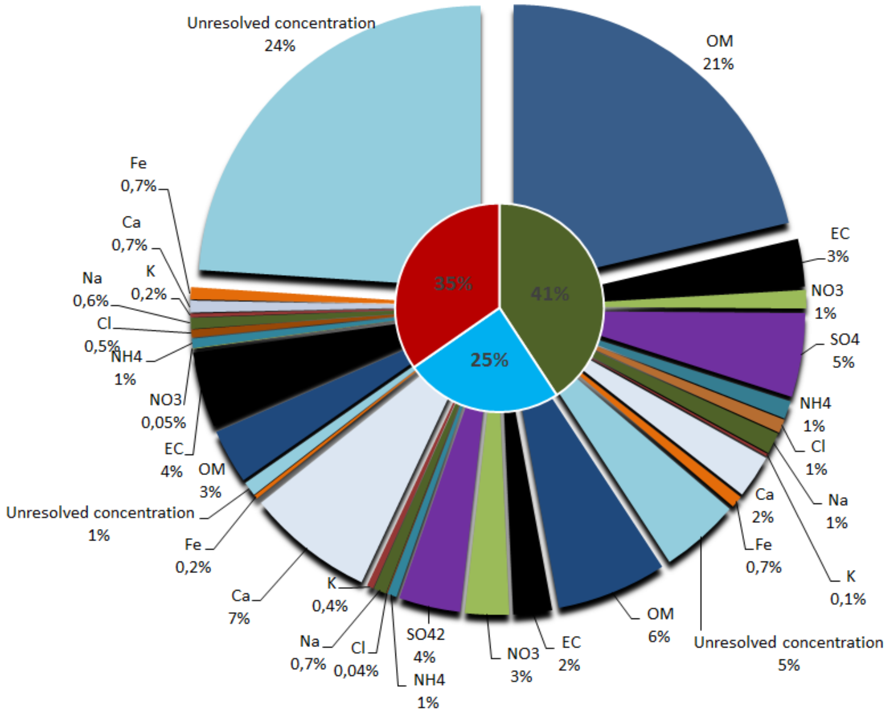
It is difficult then to define a general trend as probably the shares of each category may have a bigger contribution. However, it can be highlighted the relevant contribution of the traffic (exhaust and non-exhaust sources), the industry and household category which includes also commercial and institutional (for more information regarding the aggregated sector groups see Annex).

5.3.4 Results for Madrid

The following paragraphs report the chemical distribution of PM2.5 concentration for the summer and winter campaigns as well as the source apportionment calculated with the Lenschow approach for the city of Madrid.

5.3.5a Summer campaign results for Madrid

In Figure 5.16, the chemical contribution of the main species in each area is presented for the city of Madrid during the summer campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.16. Percentage of species contributing to the PM2.5 per source area in Madrid during the summer campaign.

As reported in Figure 5.16, the 41 % of the emissions are coming from the regional background. Organic matter has in Madrid´s regional background the biggest contribution of all the studied cities (21 %). Secondary organic aerosols (SO_4^{2-}, NO_3^- and NH_4^+) contribute in this area with a 7 % of the total PM$_{2.5}$ concentration.

The urban background station accounts for 25 % of the PM2.5 concentration. It should be highlighted the contribution of Ca^{2+} to the total share (7 %). This element forms part of the mineral dust and could have either natural or anthropogenic origin.

The traffic station represents 35 % of the chemical contribution to the PM2.5 in Madrid. Elemental carbon has in this station a bigger contribution than organic matter. The unidentified material constitutes more than 68 % of the species in this site.

5.3.5b Winter campaign results for Madrid

In Figure 5.17, the chemical contribution of the main species in each area is presented for the city of Madrid during the winter campaign. It was not possible to present a pie chart with the three stations together as only in 6 days of the winter campaign samples were collected in parallel in the urban and regional site.

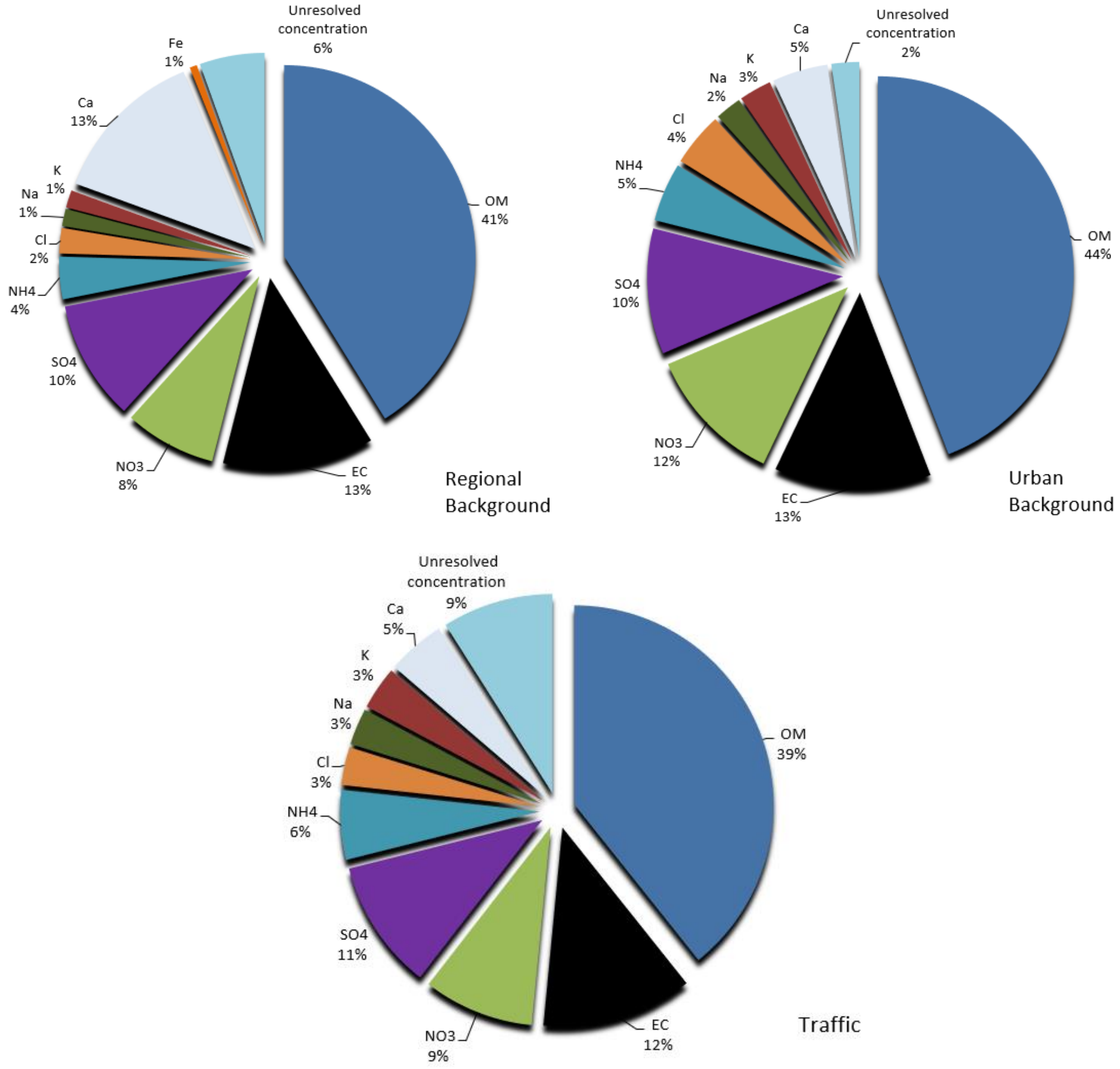


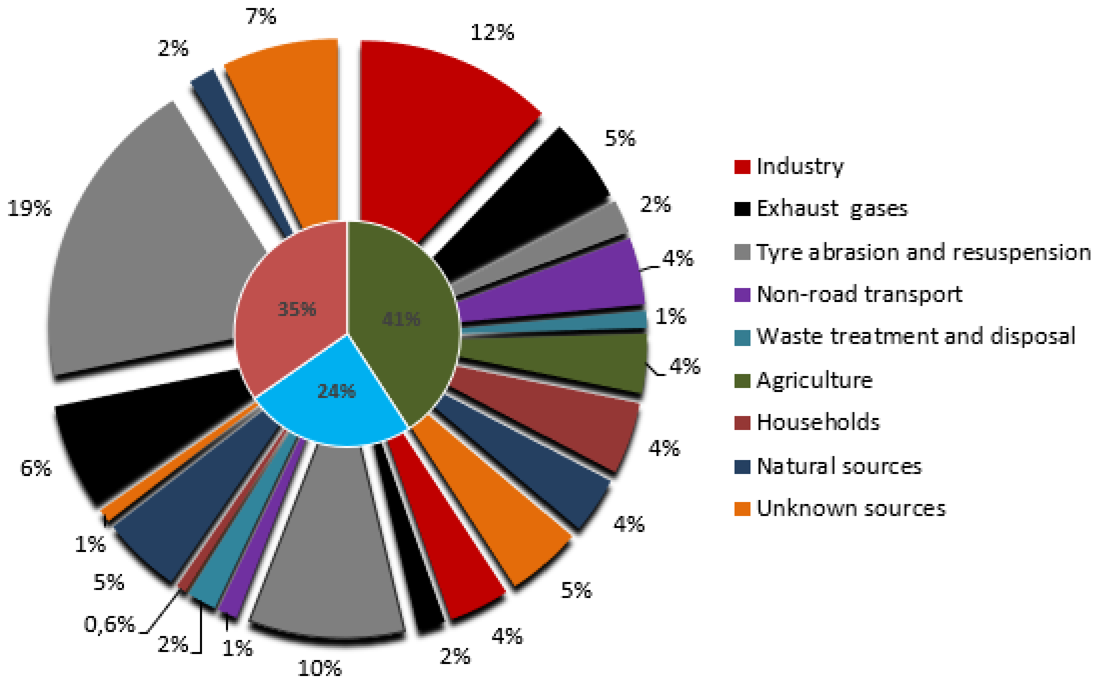
Figure 5.17. Chemical composition of PM2.5 per site in Madrid during the winter campaign.

As can be seen in Figure 5.17, organic matter shows similar contributions in the three measurement stations. However, it is worth pointing out that organic aerosols in regional areas exhibit different properties with respect to urban and traffic areas. In the former sites, organic aerosol is more oxidized than in the latter sites (Tomasi, 2016). It should be also highlighted that the elemental carbon contribution is approximately the same in the three sites. That could mean a combustion source close to the regional site. The proximity of this station to the city may also have an influence, as 7.5 km is not enough to consider this station to be representative of the regional background.

Secondary aerosols (SO_4^{2-}, NO_3^- and NH_4^+) are the major species that contributes to the PM2.5 concentration in Madrid and show similar proportions in the three stations, with slightly higher (12 %) contribution of NO_3^- in the urban site.

5.3.5c Lenschow approach results for Madrid

In order to evaluate the emission sources in Madrid only the data from the summer campaign has been used. The emission inventory data has been obtained from the “Spain´s Informative Inventory Report 1990-2016. Submission to the Secretariat of the Geneva Convention and EMEP Programme”. Emission sources for the urban area have been reported within the ICARUS Project “D2.2 Report and data on emission inventory at city level for the considered pollutants and GHGs for the years 2015, 2020 and 2030” (Neuhäuser, 2017) as well as from “Inventario de emisiones de contaminantes a la atmósfera en el municipio de Madrid 2015”. The results of the source apportionment obtained through the application of the Lenschow approach are reported in Figure 5.18 and Figure 5.19.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.18. Lenschow approach for the source apportionment of PM2.5 in the three areas in Madrid for the summer campaign.

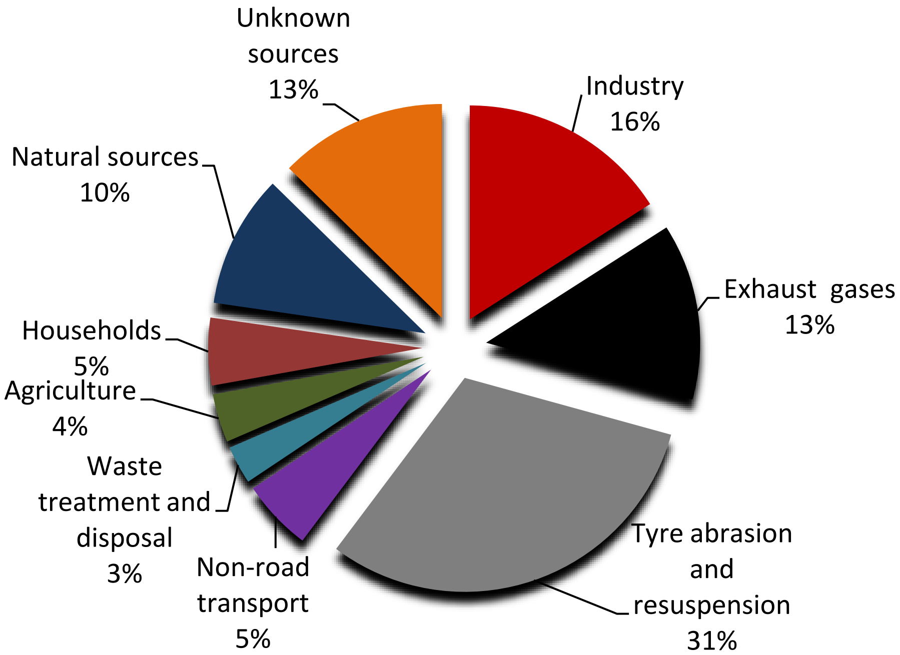


Figure 5.19. Source apportionment in Madrid per emission source for the summer campaign.

As reported in Figure 5.18, the 41 % of the sources of PM2.5 are coming from the regional background. It is also worth mentioning the contribution of the agriculture category which reaches 4 % of the total share and it is the highest together with Thessaloniki regional background. After further evaluation, it can be concluded that this contribution most likely comes from the NFR category 4F in the black carbon emission inventory, that is, from field burning of agricultural wastes in Spain.

In the urban region, the contribution of tyre abrasion and resuspension of the particles plays the main role with a 10 % of the total share of emissions.

Traffic represents the 35 % of the emission sources. 19 % of those emissions are coming from the automobile road abrasion and 6 % directly from the exhaust pipe.

In general, 44 % of the emissions in Madrid are coming from sources related with traffic (31 % from tyre abrasion and resuspension and 13 % from the exhaust pipes), as it is shown in Figure 5.19. Agriculture, mainly due to the burning of agricultural wastes accounts for the 4 % of the total emission share. Household shows a significantly lower contribution than in other cities

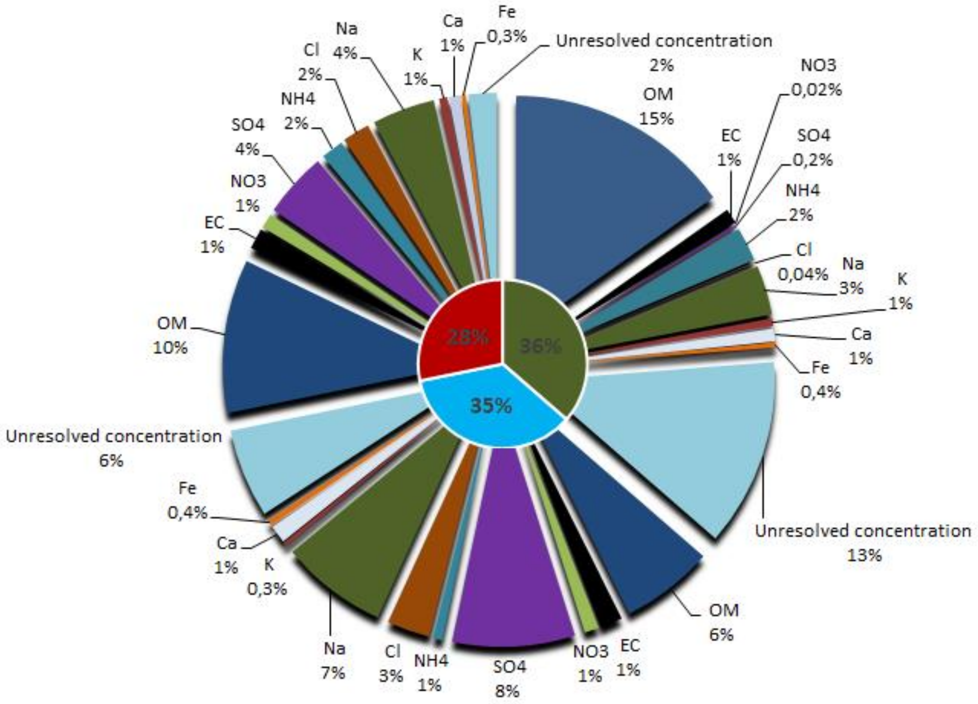
(5 %). However, the latter could be due the fact that only the summer campaign data were used when household emissions show lower values with respect to the winter period. Finally, non-road transport and waste treatment and disposal account each for 5 % and 3 % of share of emission sources, respectively.

5.3.5 Results for Thessaloniki

The following paragraphs contain the chemical distribution of PM2.5 concentration for the summer and winter campaigns as well as the source apportionment calculated with the Lenschow approach for the city of Thessaloniki.

5.3.6a Summer campaign results for Thessaloniki

In Figure 5.20, the chemical contribution of the main species in each area is presented for the city of Thessaloniki during the summer campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.20. Percentage of species contributing to the PM2.5 per source area in Thessaloniki during the summer campaign

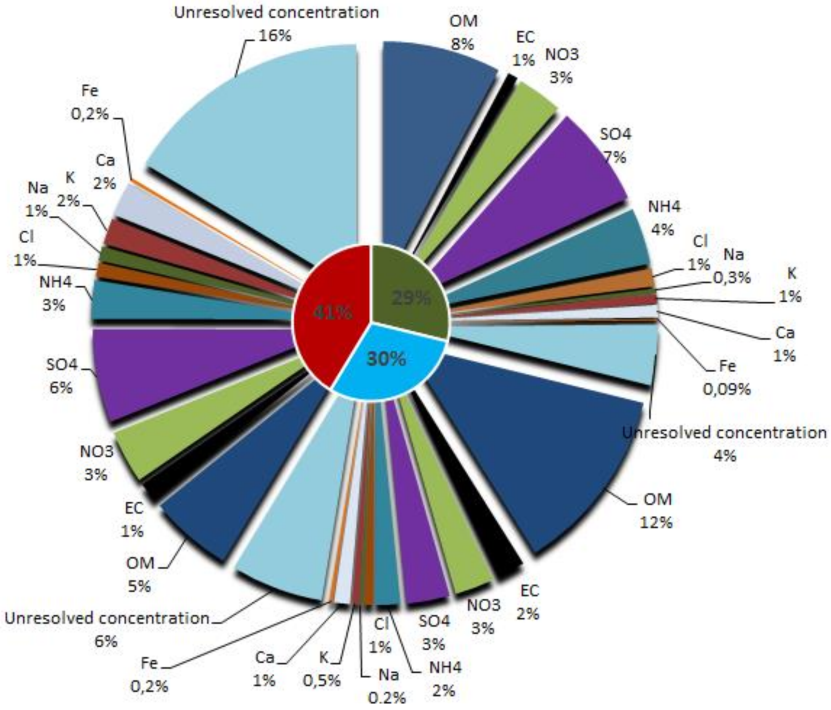
As can be seen in Figure 5.20, the regional background represents 36 % of the total share of emission sources. Its contribution is mainly formed by organic matter of natural or anthropogenic origin (15 %), unidentified material (13 %), elemental carbon from combustion sources (1 %), and organic aerosols (2 %).

During summer, the urban contribution represents 35 % of the total share of emissions. It is worth pointing out that sulphate aerosols have a higher contribution (8 %) than organic matter (6 %). It should be also highlighted that the contribution of Na^+ equal to 7 % of the total emissions in this station. This contribution may have origin from sea salts as the station is situated less than 4.5 km from the sea.

Traffic accounts for 28 % of the total emission share. The chemical distribution looks similar to the other stations. Unexpected low contribution of elemental carbon (1 %) with high contribution of sulphates (4 %) and sodium (4 %). This station is the closest to the see (less than 1 km).

5.3.6b Winter campaign results for Thessaloniki

In Figure 5.21, the chemical contribution of the main species in each area is presented for the city of Thessaloniki during the winter campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.21. Percentage of species contributing to the PM2.5 per source area in Thessaloniki during the winter campaign.

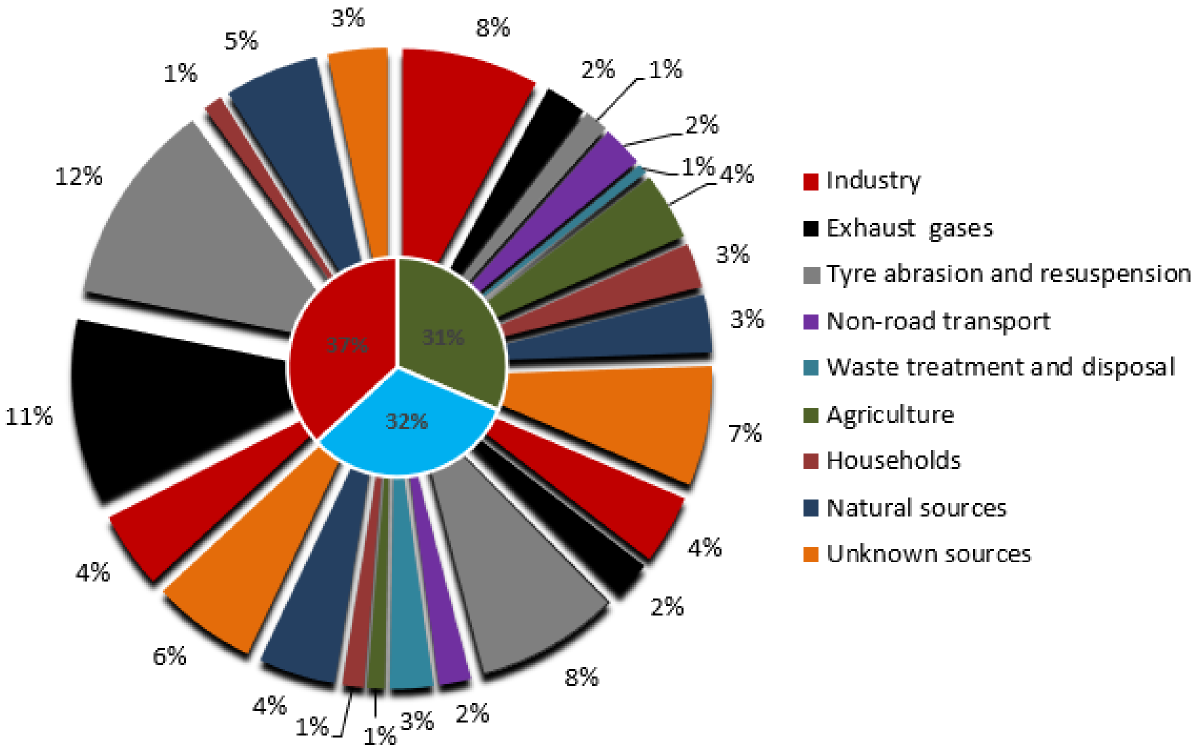
As reported in Figure 5.21, during the winter campaign the regional background station shows the lowest contribution compared to the rest of the other cities (29 %). It can be observed an increase in the nitrate aerosols contribution with respect to the summer campaign, as well as a significant increment in the proportion of sulphate aerosols. The reasons for the NO_3^- concentration increase may be due to the favourable conditions for NO_3^- formation during the cold season as low temperature and stable meteorology favour the reaction of ammonia with nitric acid to form ammonium and nitrate (Khan, 2009).

The urban background accounts for the 30 % of the total amount of emission share. It is worth pointing out the big contribution of organic matter to this section (12 %).

During the winter period the traffic station in Thessaloniki presents the biggest contribution to the total emission sources if compared to all the participating cities. A relevant part of this contribution is attributed to the unknown material (16 %). The second and the third components with the higher contribution are sulphate and organic matter with a contribution of 6 % and 5 %, respectively.

5.3.6c Lenschow approach results for Thessaloniki

In order to evaluate the emission sources in Thessaloniki data from the summer and winter campaigns has been used. The emission inventory data has been obtained from the “Greece´s Informative Inventory Report 2018. Submission under the UNECE Convention on Long-range Transboundary Air Pollution and Dir. 2004/107/EC (EU) 2016/2284 on the reduction of national emissions of certain atmospheric pollutants”. Emission sources for the urban area have been reported within the ICARUS Project “D2.2 Report and data on emission inventory at city level for the considered pollutants and GHGs for the years 2015, 2020 and 2030” (Neuhäuser, 2017) as well as from “Compilation of emission inventories for five large Mediterranean cities: Barcelona, Genoa, Marseille, Thessaloniki and Venice (2008)”. The results of the source apportionment obtained through the application of the Lenschow approach are reported in Figure 5.22 and Figure 5.23.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.22. Lenschow approach for the source apportionment of PM2.5 in the three areas in Thessaloniki.

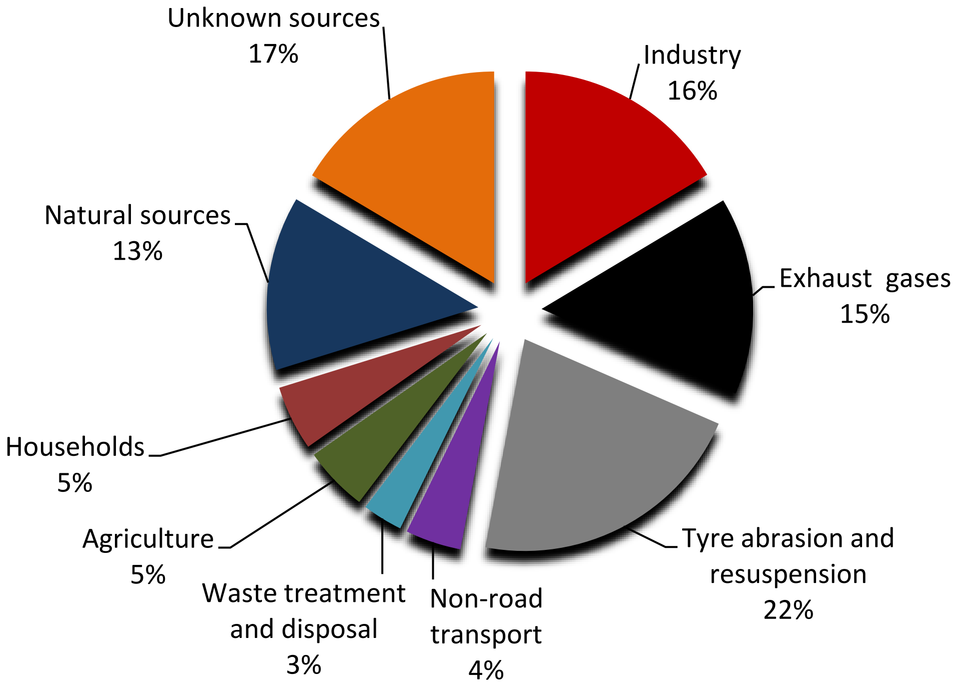


Figure 5.23. Source apportionment in Thessaloniki per emission source.

As reported in Figure 5.22, 31 % of the emissions that affect the city of Thessaloniki are coming from the regional background. A big source of pollution is agriculture with 4 % of the total emission source share. This source contribution is as high as in Madrid. Hence, the burning of agricultural waste may also have an impact in the air quality in Thessaloniki. The second group of sources is industry (8 %), followed by households (3 %).

Urban site represents for Thessaloniki the 32 % of the emission source while 8 % of the emissions are caused due to tyre abrasion and resuspension of particles in the air. It should also be highlighted that about 3 % of the emissions that contributes to the PM2.5 fraction is due to waste treatment and disposal. Also relevant for this city is the non-road-transport, mainly due to shipping and port activities (2 %).

Traffic accounts for the 37 % of the total of emission sources. It is worth mentioning the high contribution of the exhaust sources which is almost equal to the resuspension of the particles (11 % and 12 %, respectively). Natural sources have also a big impact probably due to the proximity of the Mediterranean Sea.

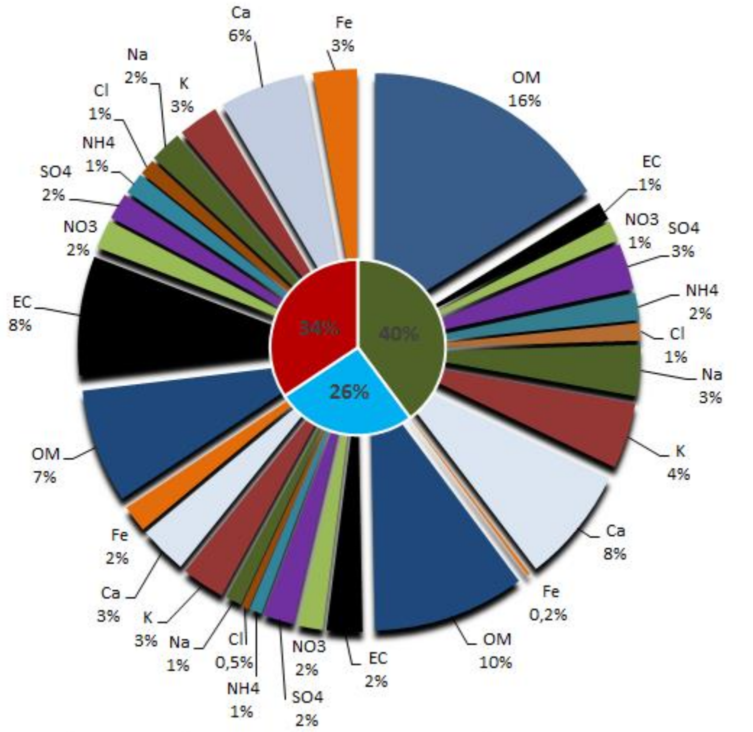
In general, 34 % of the emissions are coming from the traffic (22 % of them are non-exhaust emissions and 15 % are exhaust gas emissions). Industry plays a significant role with 16 % of the emissions as well as natural sources with a 13 %. Moreover, it should also be taken into consideration the contribution of non-road transport, mainly due to harbour activities (4 %).

5.3.6 Results for Stuttgart

The following paragraphs contain the chemical distribution of PM2.5 concentration for the summer and winter campaigns as well as the source apportionment calculated with the Lenschow approach for the city of Stuttgart. Due to a problem during the weighing process of the filters, the unresolved concentration could have not been calculated. The sum of the major species has been taken as the $PM_{2.5}$ mass. Nevertheless, the Lenschow approach has been carried out but considering that there could be a lack of material and the graphs may have higher uncertainty.

5.3.7a Summer campaign results for Stuttgart

In Figure 5.24, the chemical contribution of the main species in each area is presented for the city of Stuttgart during the summer campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.24. Percentage of species contributing to the PM2.5 per source area in Stuttgart during the summer campaign.

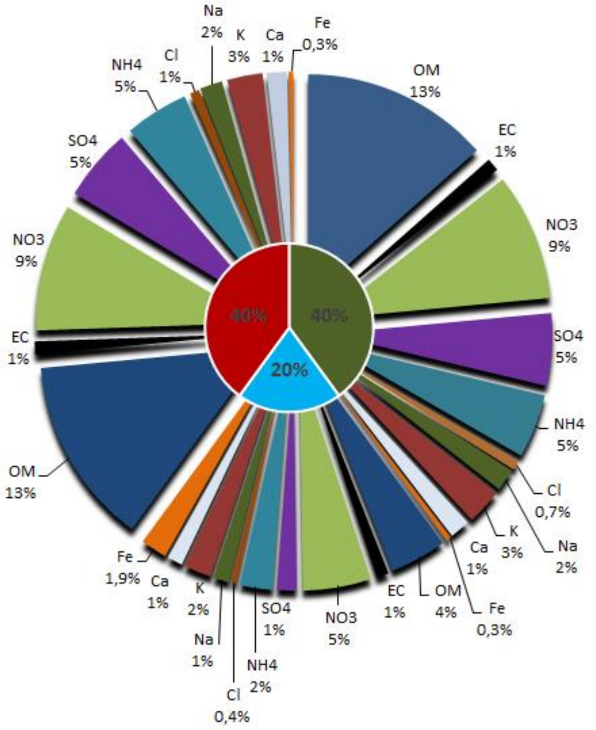
As reported in Figure 5.24, the regional background represents 40 % of the total share of emission sources. Its contribution is mainly formed of organic matter from anthropogenic or natural sources and inorganic aerosols originating from Europe-wide gaseous emissions. It is interesting to mention the contribution of calcium (8 %), potassium (4 %) and sodium (3 %).

The urban background accounts for the 26 % of the total emission share. Elemental carbon presents in the urban station higher contribution than in the regional background (1 and 2 %, respectively). There is an increase in the concentration of NO_3^- (from 1 to 2 %) and a significant decrease of the mineral dust (Ca^{2+} and K^+) with respect to the regional background station. The concentration of Fe accounts for the 2 %.

The traffic site represents 34 % of the total share of emission sources. It is interesting to observe the elemental carbon concentration (8 %) as well as the notable increase in the Fe concentration with respect to the urban background station (from 2 to 3 %).

5.3.7b Winter campaign results for Stuttgart

In Figure 5.26 the chemical contribution of the main species in each area is presented for the city of Stuttgart during the winter campaign.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.25.Percentage of species contributing to the PM2.5 per source area in Stuttgart during the winter campaign.

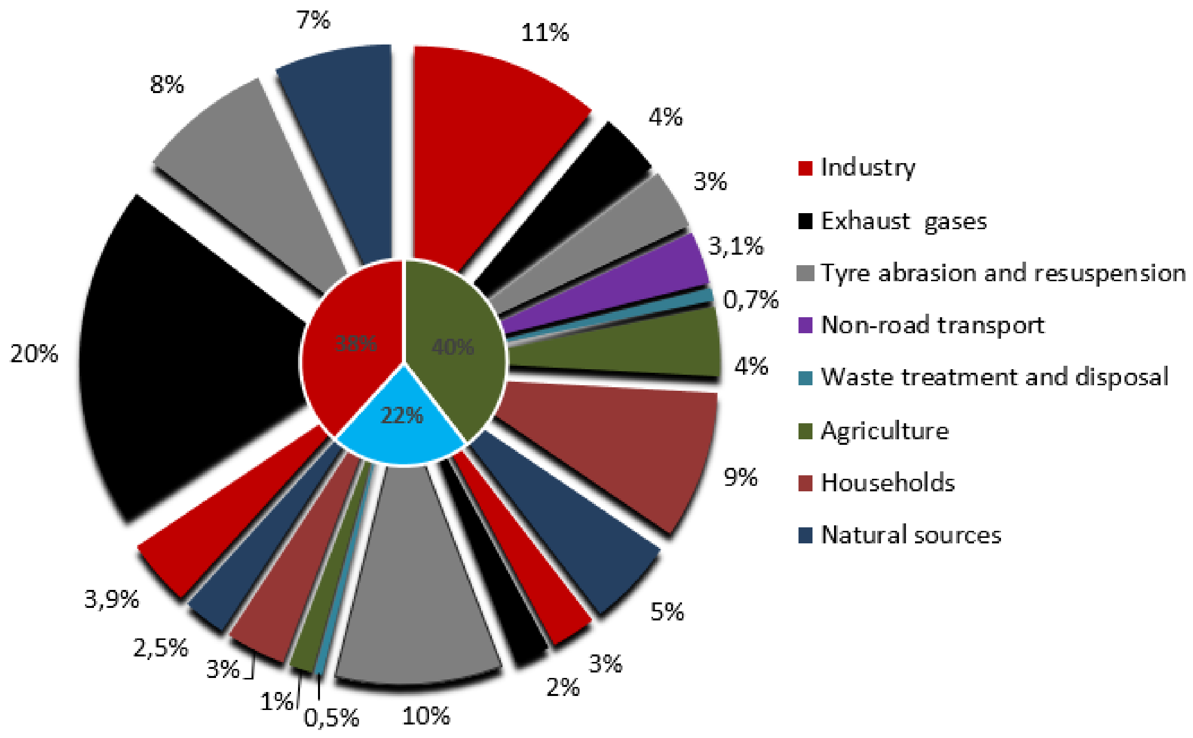
As it is shown in Figure 5.25, the regional background accounts for the same percentage in winter and in summer, that is 40 % of the total share of emission source. The main difference is the notable increase of NO_3^- concentration and the decrease in the mineral dust concentration (Ca^{2+} and K^+). It can also be highlighted the increase of SO_4^{2+} aerosol concentration with respect to the summer campaign.

The urban site contributes with the 20 % of emission sources in winter. This sector it is mainly formed of NO_3^- aerosols (5 %) and organic matter (4 %). It is worth pointing out the important amount of Fe present in this sector, almost 2 % during both campaigns.

The contribution of traffic to the total share of emission source increased with respect to the summer campaign, from 34 to 40 %. This increment has been caused by the significant increase of nitrate aerosols (from 2 to 9 %) and organic matter (from 7 to 13 %).

5.3.7c Lenschow approach results for Stuttgart

In order to evaluate the emission sources in Stuttgart the average of the two campaigns for the chemical data has been calculated. The emission inventory data has been obtained from the "National Emission Ceiling Directive (NECD) - German's National emission inventories from 1990 to 2016". Emission sources for the urban area have been reported within the ICARUS Project "D2.2 Report and data on emission inventory at city level for the considered pollutants and GHGs for the years 2015, 2020 and 2030" as well as from "Luftschadstoff-Emissioskataster Baden-Württemberg 2014". The results of the source apportionment obtained through the application of the Lenschow approach are reported in Figure 5.26 and Figure 5.27. It has to be kept in mind that no unresolved concentration has been used. This leads to an underestimation of the category tyre abrasion and resuspension in the traffic site.



Areas shown in the inner sector diagram: in red traffic site, in blue UB; and in green RB.

Figure 5.26 Lenschow approach for the source apportionment of PM2.5 in the three areas in Stuttgart.

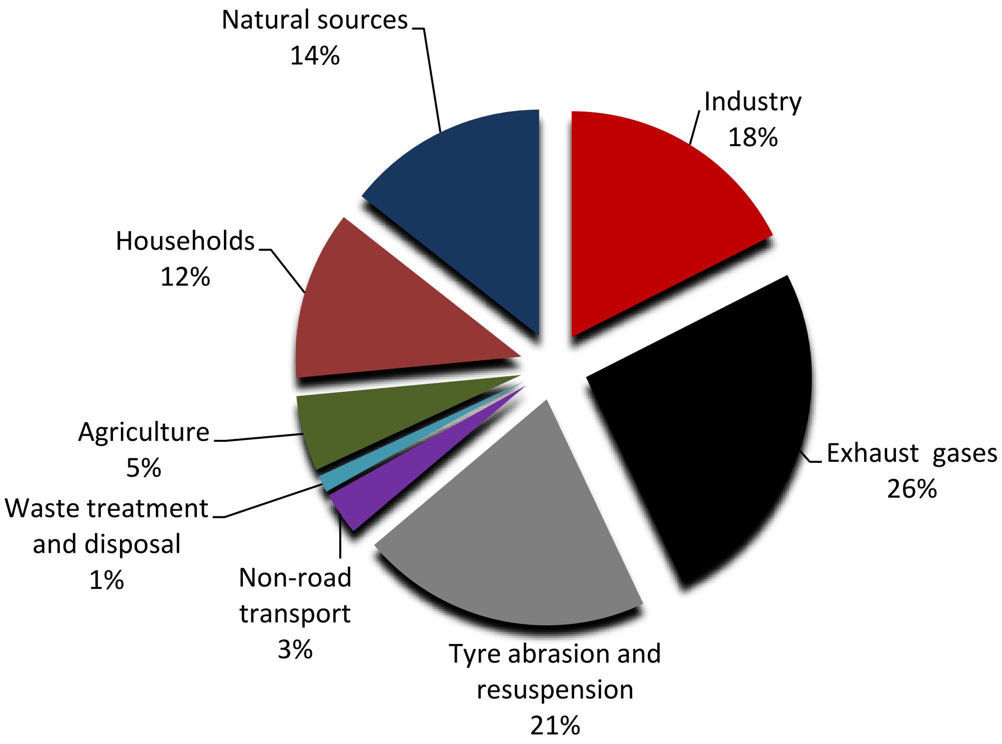


Figure 5.27.Source apportionment in Stuttgart per emission source.

As reported in Figure 5.26, the 40 % of the emission sources are coming from the regional background. It is considerably high the amount of emissions coming from industry (11 %) as well from households category (9 %) due to biomass burning.

The urban background represents 22 % of the total emission source. It should be highlighted the automobile road abrasion accounts for 10 % of the emissions in this site.

The traffic site contributes with 38 % of the total emission sources. Although it can be seen in Figure 5.26 that the exhaust sources category has the highest contribution, it should be noticed that this is due to the lack of unresolved material, based on the assumptions made in traffic stations to suppose that 70 % of the unresolved material is coming from the resuspension of the road and the abrasion of brakes and tyres (Quass, U., 2007).

In general, as can be seen in Figure 5.27, traffic represents the biggest source of emissions (47 %) of PM2.5. The second group are the natural sources (14 %) followed by the industry (18 %). Household category represents also a major source of emissions contributing to 12 % of the total. Waste treatment and disposal and non- road transport do not show a big contribution (1 and 3 %, respectively).

6 Positive Matrix Factorization

6.1 Mathematical background for Positive Matrix Factorization method

Positive Matrix Factorization (PMF) is a method that aims to solve Equation 2.1 by decomposing the matrix of speciated data (X) into two matrices: factor contributions (G) and factor profiles (F) as shown in Equation 6.1 (Norris, 2014).

$$X = GF + E \qquad \text{Equation 6.1}$$

The matrix E corresponds to the residual matrix, in other words, the difference between the measurement X and the model Y as a function of factors G and F, as shown in Equation 6.2.

$$E = e_{ij} = X - GF = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \qquad \text{Equation 6.2}$$

The objective of PMF is to identify the number of factors p and the species profile of each source f_{ij} and the amount of mass contributed by each factor to each individual sample g_{ij}. These factor profiles f_{ij} need to be interpreted by the user to identify the source types.

In order to find the factor contributions and profiles, PMF minimizes the sum of the squares of the residuals weighted inversely with the uncertainties of the data points by using the objective function Q, as shown in Equation 6.3.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \qquad \text{Equation 6.3}$$

With u_{ij} the uncertainties of the species.

PMF constrains all the elements of G and F to be non-negative. Hence, sources cannot have negative species concentration ($f_{kj} \geq 0$) and samples cannot have a negative source contribution ($g_{ik} \geq 0$). However, these conditions are not enough to avoid rotations in the space of the solution and further analysis are needed to find a solution with physical meaning.

Q is a critical parameter for PMF. Two versions of Q are displayed for the model runs:

- Q(true) is the goodness-of-fit parameter calculated including all points.
- Q(robust) is the goodness-of-fit parameter calculated excluding points not fit by the model, defined as samples for which the uncertainty-scaled residual is greater than 4.

The difference between Q(true) and Q(robust) is a measure of the impact of data points with high scaled residuals. These data points may be associated with peak impacts from sources that are not consistently present during the sampling period. In addition, the uncertainties may be too high, which result in similar Q(true) and Q(robust) values because the residuals are scaled by the uncertainty (Norris, 2014). A theoretical Q-value can be calculated as shown in Equation 6.4.

$$Q_{theoretical} = nm - p(n + m) \qquad \text{Equation 6.4}$$

Where *n* is the number of species, *m* is the number of samples and *p* the number of factors. The differences of Q-values obtained with different number of factors are useful indicators of the physical meaning of the result. If introducing another factor lowers the Q-value only by the number of additional factor elements, then the introduced factor should be rejected (Belis et al, 2014) as one factor could have been split into two factors with no physical meaning.

The model uses consecutive iterations to find the lowest Q (robust) values, which is the best solution. However, it could be that the model reaches a local minimum instead of a global minimum. To avoid that and maximize the chance of reaching a global minimum the model should be run 20 times developing a solution and 100 times for a final solution, each time with a different starting point (Norris, 2014).

Further information can be found in Paatero (1997), Paatero and Hokpe (2009) and the EPA PFM 5.0 User Guide (Norris, 2014).

6.2 Preliminary input data analysis and further considerations

The EPA PMF 5.0 software was run for each sampling site (regional background, urban background and traffic site) in the six participating cities (Athens, Brno, Ljubljana, Madrid, Thessaloniki and Stuttgart) using the combined data of the winter and the summer campaign.

The chemical composition of the data sets was used, namely cations, anions, metals, OC/EC and PAHs (if available), including the total mass concentration of the PM2.5. Each of the species can be seen in Table 3.2.

Before running the model, summary plots were checked to gain an overview of the relationships between variables and their temporal evolution. This is particularly useful to identify anomalous data points (outliers) that can be excluded before running the model.

To avoid double counting, either the ion of the elemental form was included, that is chloride (Cl^-) or Cl, water-soluble potassium (K^+) or K, sodium ion (Na^+) or Na, calcium ion (Ca^{2+}) or Ca and sulphate (SO_4^{2-}) or S. In general, the form that was better fitted by the model was used (higher r^2). Concentration data below the detection limit has been substituted with half of the detection limit. Missing values have been replaced by the median value of each specie. An extra model uncertainty of 10 % was added (Norris, 2014).

Other tool that has been used to analyse the input data has been the signal-to-noise (S/N) ratio. The signal-to-noise ratio (S/N) is defined as the power ratio between a desired signal (S, meaningful information) and the background noise (N, unwanted signal). Species with a signal-to-noise lower than 0,2 were excluded from the model and categorised as “bad species”. Variables with a S/N ratio falling between 0,2 and 2,0 have been labelled as “weak species” but were still suitable for the analysis. “Strong species” were those with a S/N ratio greater than 2,0. However, some species have been downweighed to weak or bad species after analysing the residuals and the data fit of the model.

Scaled residuals are also useful in selecting the final number of factors. These residuals should be symmetrically distributed within a range of -3 to +3 (and preferably less). If the scaled residuals are too large (<< -3 or >> +3) for certain species, it could be that the uncertainty specified for that species are too small, that the model is not fitting the species or that the species is present in an infrequent source. If the scaled residuals are especially small (close to zero) for one variable, then either overly large uncertainties have been specified or this variable is explained by a unique factor.

Several factors (from 3 up to 9 factors) were run for each data set, choosing the solution with better physical meaning and better stability (less rotational ambiguity) as factor analysis can give a number of possible solutions that are mathematically correct, meaning that there is not a unique solution. Variability and uncertainty in the PMF solution can be estimated using three methods (Norris, 2014):

- Displacement (DISP) analysis helps the user understand the selected solution in finer detail, including its sensitivity to small changes. It includes effects of rotational ambiguity but do not include effects of random errors in the data.

- Bootstrap (BS) analysis detects deviation or various percentiles of factor profiles (F-matrix values) from numerous bootstrap runs. It is used to identify whether there are a small set of observations that can disproportionately influence the solution. Bootstrap error intervals include effects from random errors and partially include effects of rotational ambiguity. For this work, 100 bootstrap runs were performed with a minimum correlation of 0,6. The solution was set as valid only when minimum 80% of the factors were mapped.

- BS-DISP is a hybrid method to determine the effects of random errors and rotational ambiguity.

PMF rotations can also be controlled by imposing external information. Certain trace elements can be constrained to a profile factor when additional information about the source composition is known. In table6.1, the tracer elements of the most common sources categories are listed (Bari A. , 2009).

Table 6.1. Tracers for the most common PM sources.

Source		Trace compounds
Traffic	Exhaust (EX)	Elemental carbon, organic carbon, anthanthrene, fluoranthene, retene (diesel cars) dibenzo(ah)anthracene, perylene (gasoline combustion)
	Non-exhaust (NEX)	Zn, Ca (lubricating oil combustion), Zn (tyre wear), Cu, Ba, Sb (brake wear), Fe, Ca, Al (mineral road dust), PAHs
Heavy oil combustion		V, Ni, SO_4^{2-}, OC, EC, anthracene, fluoranthrene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene,
Biomass burning		OC, EC, K^+, K, PAHs, Zn, Br, Pb benzo(ghi)pyrene, indeno(123-cd)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene,
Industrial emissions		depending on industrial processes Zn, Pb, S, Cu, Cd, Sb, Mn/Ca (metallurgical/cement industry)
Seconary aerosol	Sulfate	SO_4^{2-} (or S), NH_4^+, OC (if secondary organics are included)
	Nitrate	$NO3^-$, NH_4^+, OC (if secondary organics are included)
Mineral dust		Al, Si, Ca, Fe, K, Ti, Sr, Mg
Sea salt	Fresh	Na^+, Cl^-, Mg^+
	Aged	Na^+, Mg^+, NO_3^-
Fireworks		K, Cu, Zn, Pb, Mg, Cl, SO_4^{2-},Ca, Si

6.3 PMF Results

6.3.1 Results for Athens

6.3.1a Athens regional background

The results for the species contribution in each source in the regional background measurement station in Athens can be seen in Figure 6.1. Six sources have been identified by using 72 samples and 19 species. Constrains for calcium have been used under the limitation dQ %< 0,5 for the factor Traffic EX (pull down maximally) and the factor Mineral dust (pull up maximally).

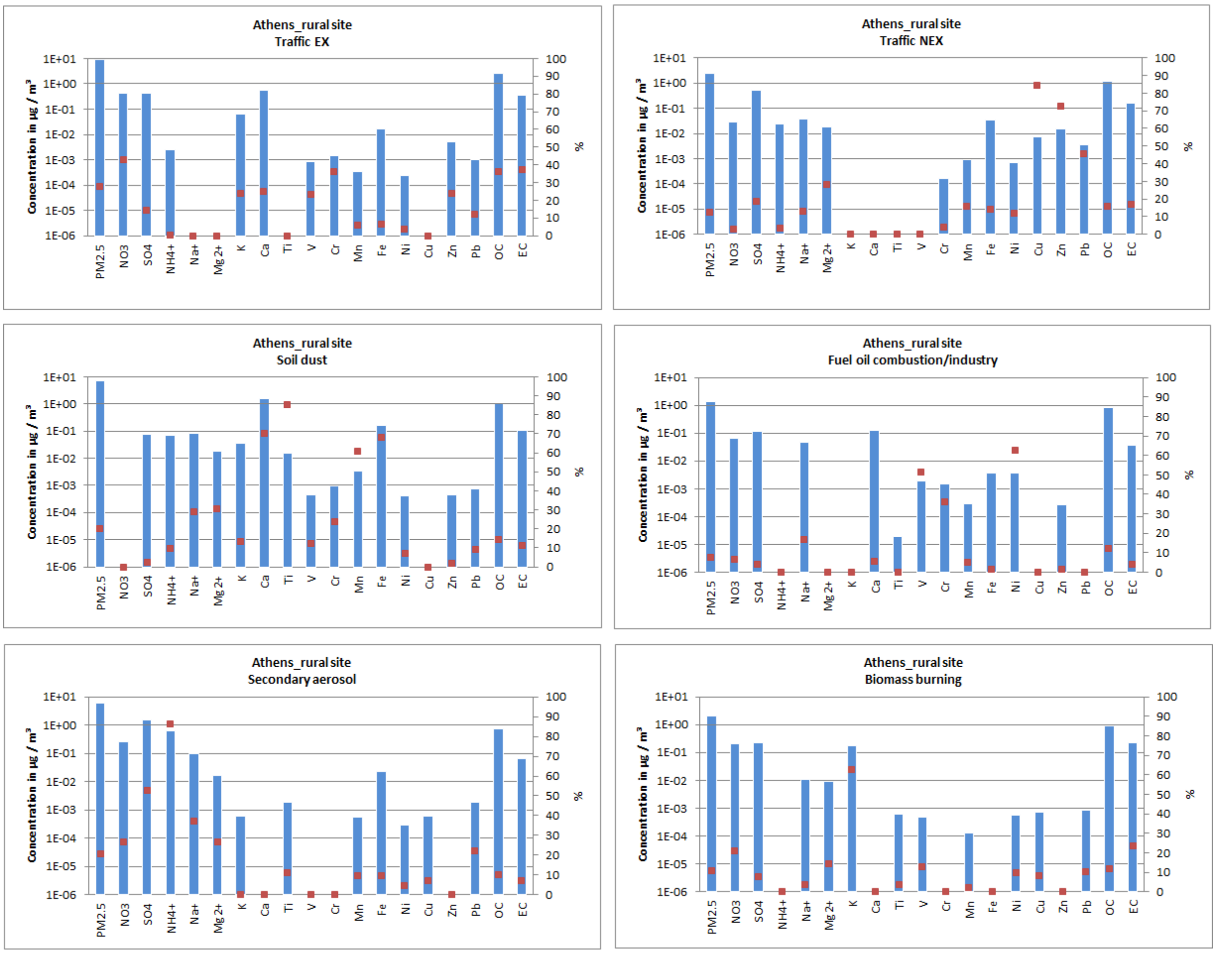


Figure 6.1. Factor profiles in µg m^{-3} and percentage of contribution of the species for the regional background site in Athens.

As can be seen in Figure 6.1, two different sources related to traffic emissions have been identified. On one side, high percentage of emission such as OC and EC coming directly from the exhaust sources (Traffic EX). According to some studies, a OC/EC ratio close to 1 indicates an exhaust gas source (El Haddad et al., 2009; Amato et al., 2011; Waked et al., 2014) On the other side, non-exhaust traffic emissions (traffic NEX) such as Zn and Cu. The source of this emissions are the brake wear and the additives for the lubricating oil.

High shares of EC and K denote the presence of a biomass combustion source. The temporal variation of its contribution between the winter and summer campaign can be clear seen in Figure 6.2 (green line). Biomass burning accounts for the 13 % of the total mass of PM2.5 in this measurement site. This percentage is smaller than expected which means that it could be that part of the carbon and the K coming from this source have been instead identified as traffic EX which has a considerably high percentage (34 %), as can be seen in Figure 6.3.

A high contribution of NH_4^+ and SO_4^{2-} characterize a secondary sulphate source. It accounts for 21 % of the total mass concentration of PM2.5 and remains stable during both campaigns (no seasonal variation).

7 % of the total mass of PM2.5 corresponds to the residential fuel combustion source. This source has been traced by high mass contribution of V and Ni. A seasonal variation cannot be appreciated. This could be due to the fact that industry emissions produced during the whole year are usually coupled to this source.

One more factor have been identified as mineral dust thanks to key components like Ti, Fe and Mg^{2+}. In general, it contributes with 20 % to the emission sources of PM2.5. In Figure 6.2. This source shows a low contribution except for peaks during February that could correspond with dust events in Greece.

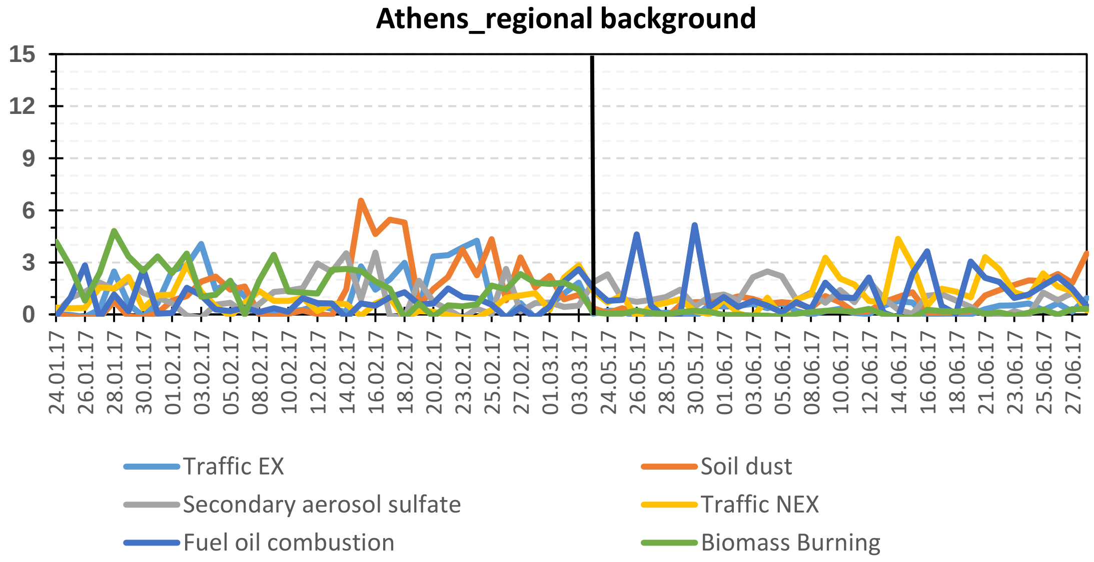


Figure 6.2. Temporal variation of normalized factor contribution for Athens regional background.

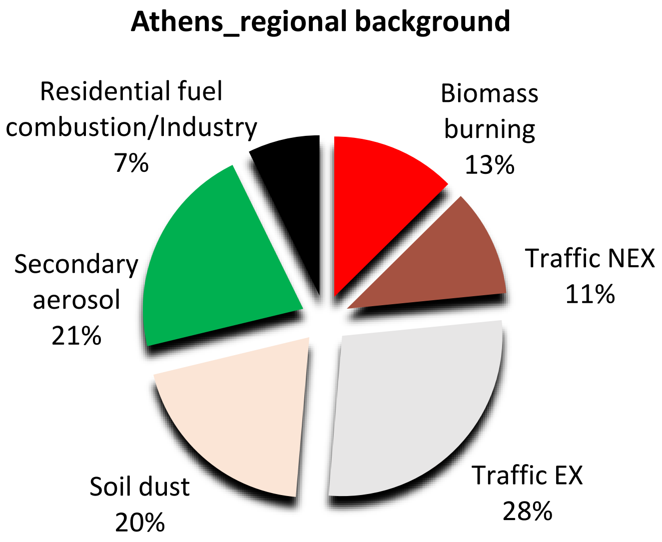


Figure 6.3. Source contribution of the six factors to the measured PM2.5 concentration for the regional site in Athens in percentage.

6.3.1b Athens urban background

The results for the species contribution in each source in the urban background measurement station in Athens can be seen in Figure 6.4. Seven sources have been identified by using 68 samples and 19 species. Constrains for potassium have been used under the limitation dQ %< 0,5 for the factor Traffic NEX (pull down maximally) and the factor biomass burning (pull up maximally). Moreover, a constraint for naphthalene has also been used in regard to his contribution to the source secondary aerosol (pull down maximally).

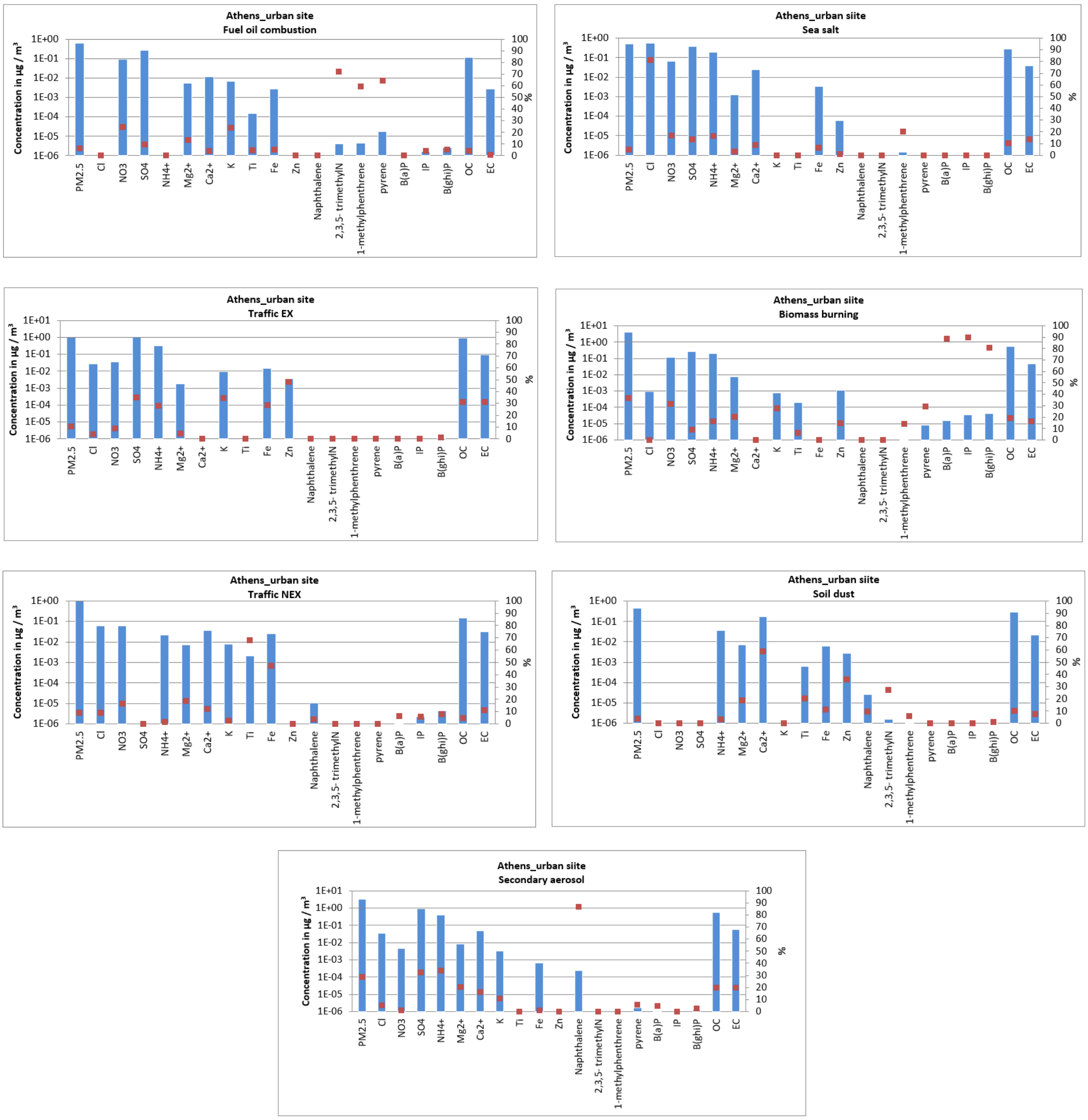


Figure 6.4. Factor profiles in μg m^{-3} and percentage of contribution of the species for the urban background site in Athens.

As can be seen in Figure 6.4, fuel oil combustion have been traced by the PAHs. 1-methylphenthrene; 2,3,5- trimethylnaphthalene and pyrene. There are two sources with significant PAHs contributions. The other source emits heavier PAHs namely, benzo(a)pyrene, indeno(1,2,3 - c,d)pyrene, and benzo(ghi)perylene, which are characteristically found during the biomass burning. As can be seen in Figure 6.5, the contribution of this source drops during summer and it contributes to 37 % of the total amount of PM2.5 (see Figure 6.6).

The source coming from the exhaust sources have been identified by the ratio OC/EC which should be close to 1 according to the references (El Haddad et al., 2009; Amato et al., 2011; Waked et al., 2014). It contributes with 10 % to the total amount of PM2.5 emission sources. On the other side, the non-exhaust traffic emissions have been distinguished by high concentration of Fe and Ti. The total contribution of the traffic to the emissions of PM2.5 is 19 %, lower than in the regional background site. Both sources have a stable trend through the year with an exception in the traffic NEX category on the 6/2/2017 due to probably a dust event.

The fifth factor has a high concentration of Ca^{2+} and is suggested to be associated with emissions from soil dust. This source contributes with a 4 % of the total amount of sources of PM2.5 and does not present temporal variation.

The sixth factor is distinguished by high concentrations of Cl^{-} and is suggested to be particles coming from sea salt. Its source contribution is a 5 % of the total and shows higher contribution in summer than in winter.

The last factor corresponds to the formation of secondary sulphate aerosols, traced by high amounts of NH$_4^+$ and SO$_4^{2-}$. It includes a small amount of OC, which is also considered to be secondary OC. It does not present seasonal variation and it contributes with a 29 % of the total emission sources of PM2.5.

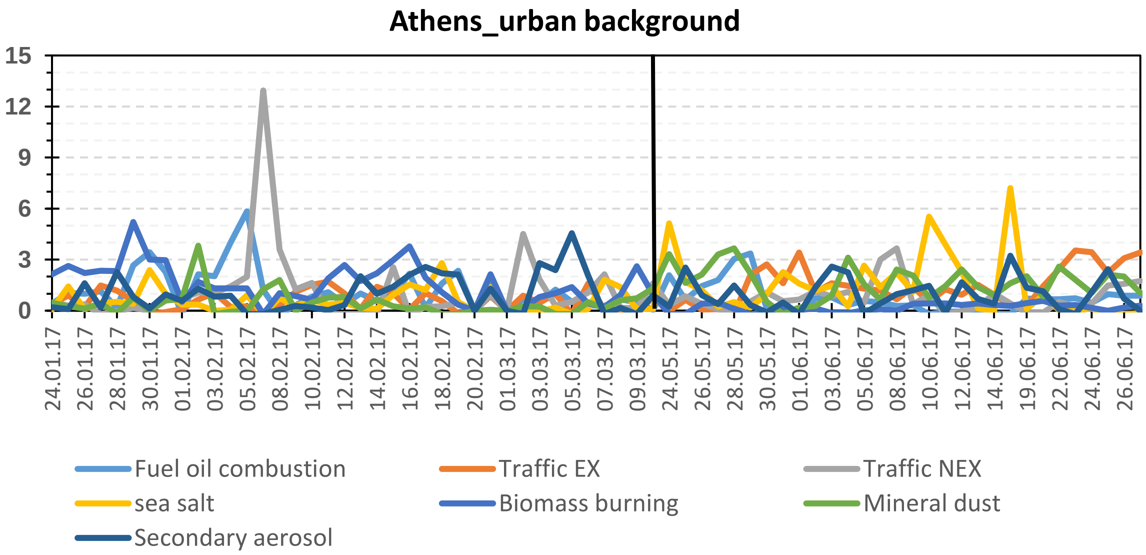


Figure 6.5. Temporal variation of normalized factor contribution for Athens urban background.

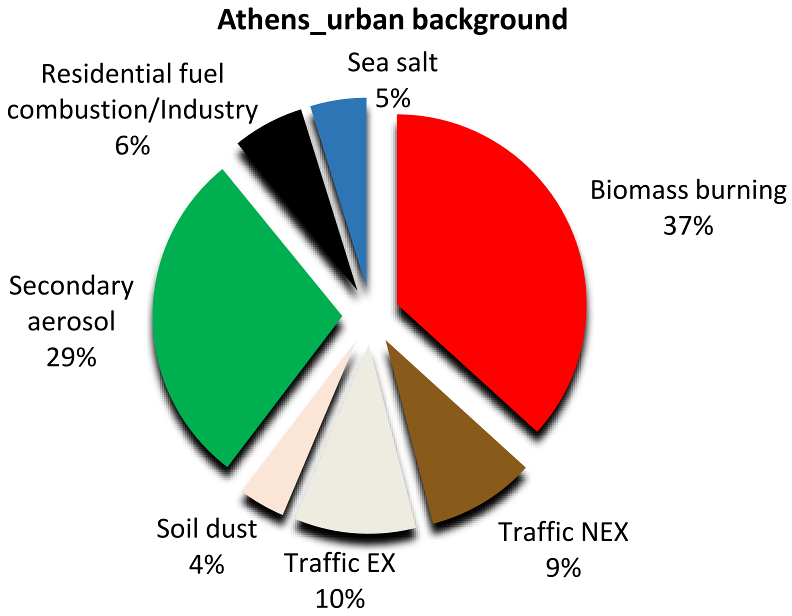


Figure 6.6. Source contribution of the seven factors to the measured PM2.5 concentration for the urban background site in Athens in percentage.

6.3.1c Athens traffic site

The results for the species contribution in each source in the traffic measurement station in Athens can be seen in Figure 6.7. Six sources have been identified by using 74 samples and 25 species.

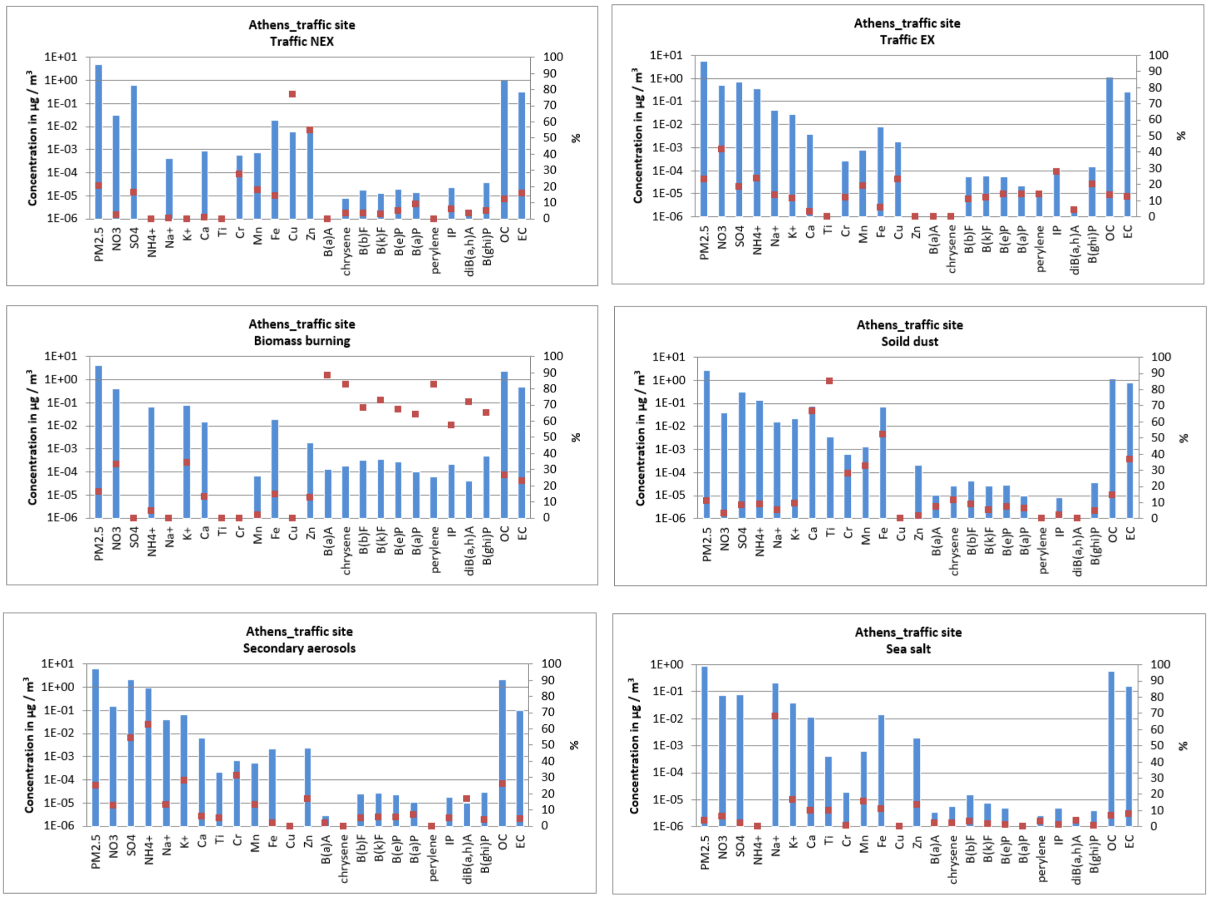


Figure 6.7. Factor profiles in μg m^3 and percentage of contribution of the species for the traffic site in Athens.

As can be seen in Figure 6.9 traffic-related emissions of PM2.5 account for 43 % of the total source contribution. The non-exhaust source contributes 23 % of the total and have been traced by high loadings for Cu and Zn that come mainly from tyre and brake wear. The pollutants that come directly from the exhaust pipe represent the 20 % of the PM2.5 mass in this site and have been associated with the presence of OC/EC in a ratio 1 to 1 and PAHs. As can be seen in Figure 6.8, the traffic related sources do not present seasonal variation except for a peak on the 27/2/17 for the traffic EX.

Biomass burning is the only source that shows a seasonal variation in the traffic site in Athens, as can be seen in Figure 6.8It can be distinguished by traces of K, OC, EC and PAHs. It accounts for 17 % of the total mass of PM2.5.

High loadings for Ca and Ti denote the presence of mineral dust as a source of PM2.5. The contribution of this source to the PM2.5 mass is 11 %. As can be seen in Figure 6.8, a dust event on the 2/7/17 occurred. The rest of the measurement campaign remained stable.

The fifth factor is distinguished by high concentrations of $SO_4^{2-}$and NH_4^+, suggesting that it is a source associated with the formation of secondary sulphate aerosol. It accounts for the 25 % of the total source contribution to the mass of PM2.5.

A small contribution (4 %) to the PM2.5 mass have been found to be sea salt by tracing high loadings for Na^+. This source does not present seasonal variation.

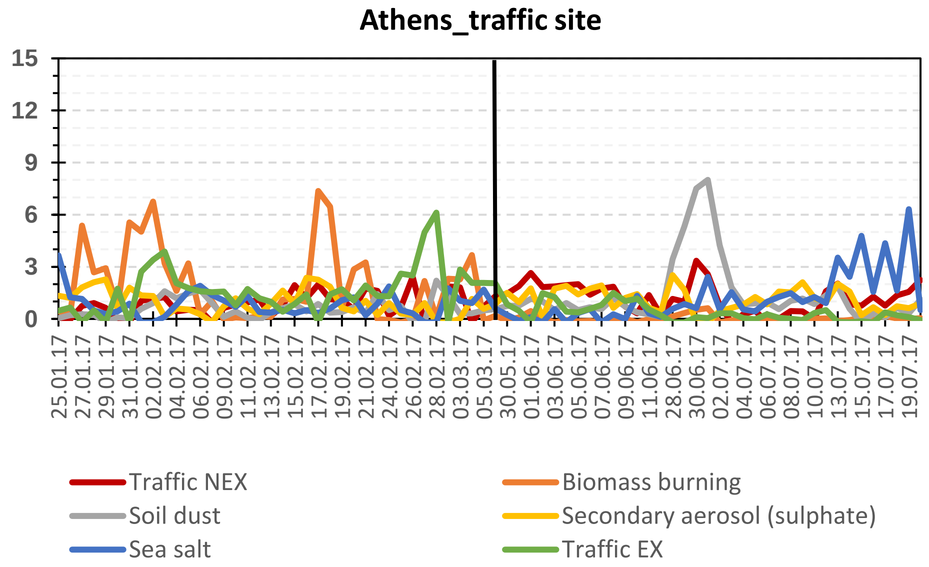


Figure 6.8. Temporal variation of normalized factor contribution for Athens traffic site.

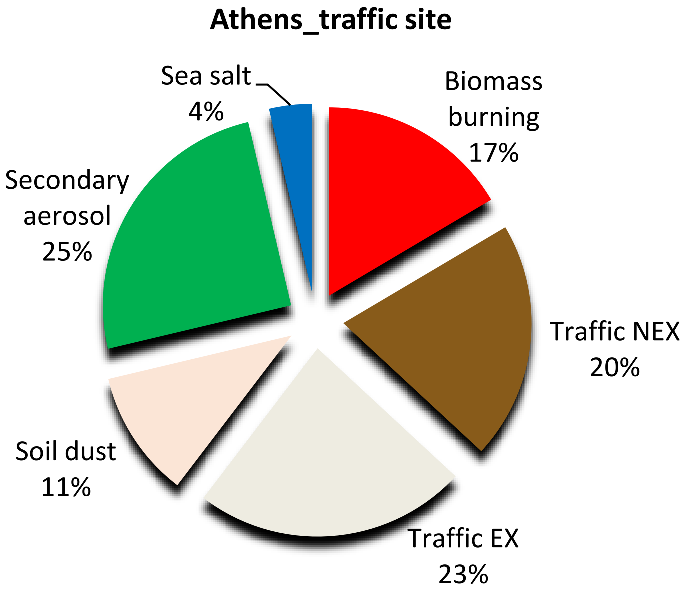


Figure 6.9. Source contribution of the six factors to the measured PM2.5 concentration for the traffic site in Athens in percentage.

6.3.2 Results for Brno

6.3.2a Brno regional background

The results for the species contribution in each source in the regional background measurement station in Brno can be seen in Figure 6.10. Five sources have been identified by using 60 samples and 12 species.

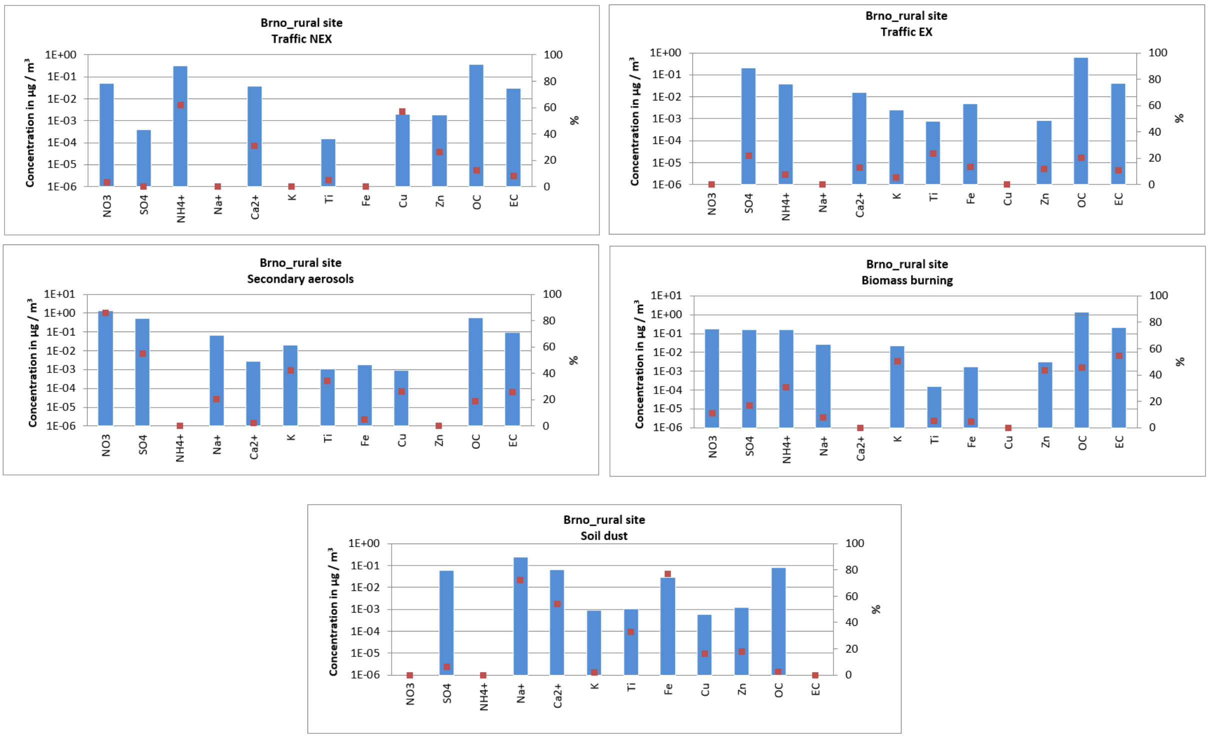


Figure 6.10. Factor profiles in µg m^{-3} and percentage of contribution of the species for the regional background site in Brno.

As can be seen in Figure 6.10, the first factor exhibits high loading for Cu, which is associated with traffic non-exhaust sources due to brake wear. The contribution of the traffic exhaust to the PM2.5 mass in the rural background is 12 %. The pollution coming from the exhaust sources haven been traced by high loadings for OC and EC. It presents a contribution to the PM2.5 of 13 %. No seasonal variation is shown in for the traffic related sources.

The third factor correlates strongly with NO_3^- and SO_4^{2-}, consistent with source categories related to secondary particles (secondary sulfate and secondary nitrate). It includes an amount of OC, which is also considered to be secondary OC. It presents the highest contribution as a source of PM 2.5, 38 %, as can be seen in Figure 6.12.

In fourth factor, relatively higher loadings for K and carbonaceous species were observed which might indicate biomass combustion as the source category. The seasonal variation of this source can be clearly identified in Figure 6.11. This source represents the 30 % of the total source contribution to PM2.5, as can be seen in Figure 6.12.

The last factor corresponds to the source soil dust. This source has been traced by high loading for Ca^{2+} and Fe. In Figure 6.11, a peak on the temporal normalized contribution is observed on the 15/06/2017. This peak is due to an increase of the Fe concentration in the PM2.5 total mass. The concentration of Ca^{2+} was also higher than the average during those days, indicating that a dust event could have been taken place.

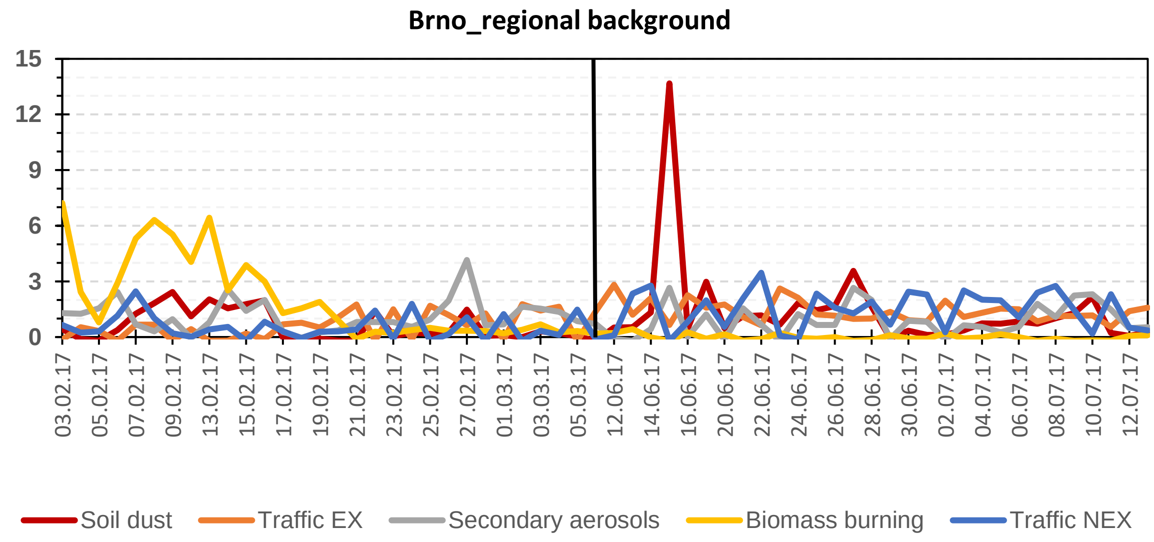


Figure 6.11. Temporal variation of normalized factor contribution for Brno regional background.

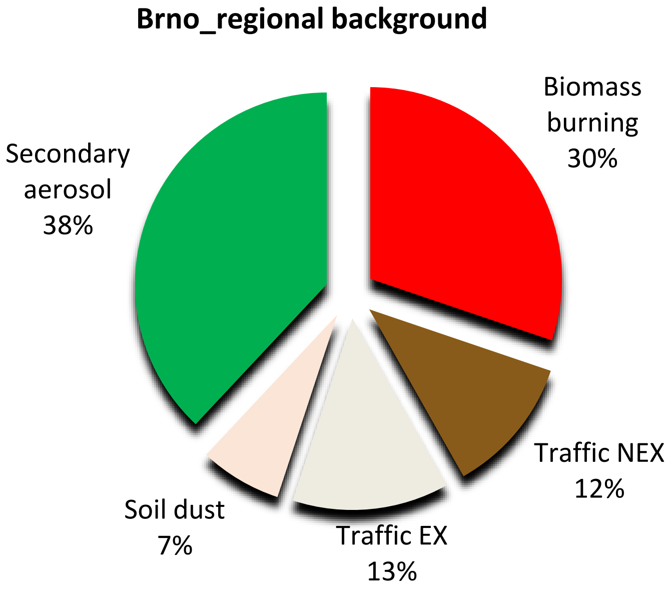


Figure 6.12. Source contribution of the five factors to the measured PM2.5 concentration for the regional background site in Brno in percentage.

6.3.2b Brno urban background

The results for the species contribution in each source in the urban background measurement station in Brno can be seen in Figure 6.13. Six sources have been identified by using 60 samples and 16 species.

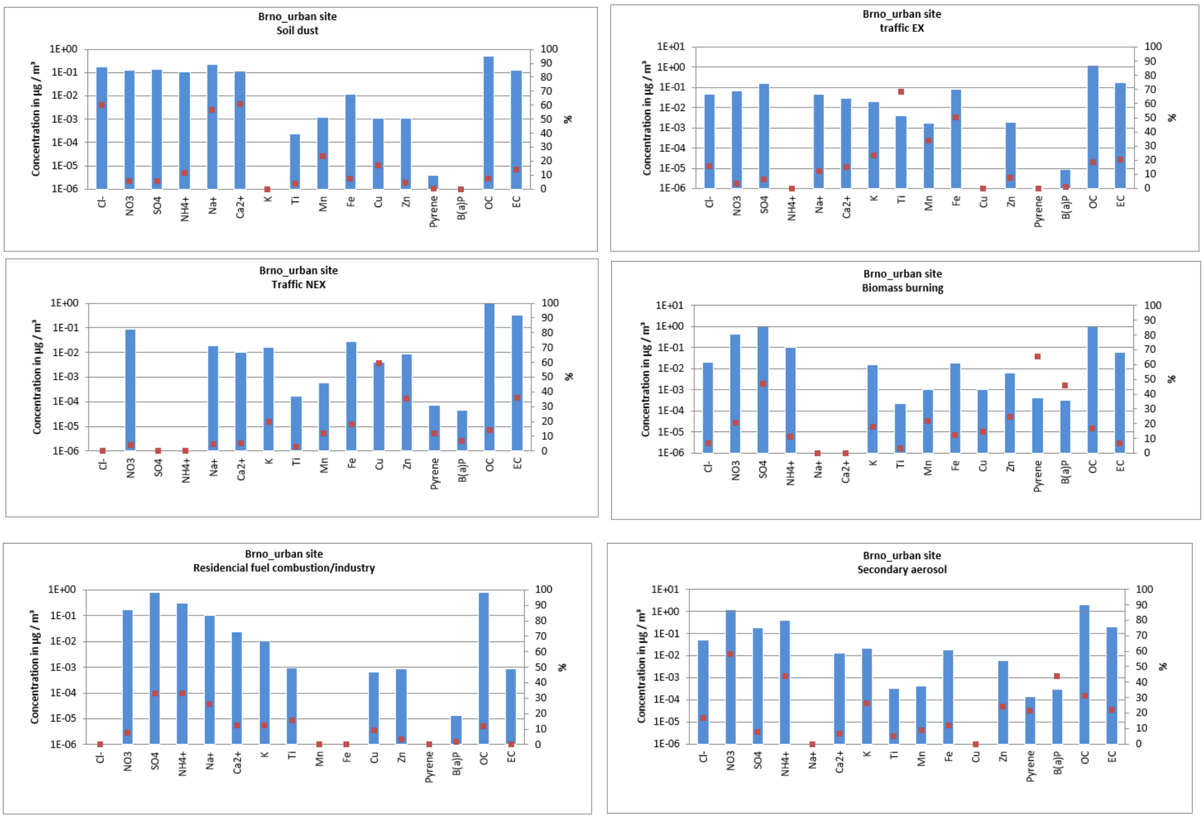


Figure 6.13. Factor profiles in µg m^{-3} and percentage of contribution of the species for the urban background site in Brno.

The first factor exhibits high loadings for Ca^{2+} which is associated with crustal dust. It is worthy to mentioning the contribution of Cl^- and Na^+ to this source, probably due to the road salt in winter that would explain the different in the contribution of this source between summer and winter, as it can be seen in Figure 6.14. The contribution of this source to the PM2.5 mass concentration is 11 %, as shown in Figure 6.15

The traffic exhaust source has been traced by a ratio OC/EC close to one. However, this factor also presents high contribution of Ti and Fe, tracers of non-exhaust traffic pollution. This is because positive matrix factorisation extracts source profiles and quantifies contributions based on the temporal variation of the chemical species so the one with the same emission pattern might be identified as coming from the same factor.

Biomass burning (21 % of $PM_{2.5}$) have been identified by the K and the high loads of PAHs. As can be seen in Figure 6.14, this source presents a clear seasonal variation which peaks in winter and drops dramatically in the summer months. Fuel combustion also presents this seasonal variation. However, the decrease is not that marked as part of the pollutants associated with this source are coming from the industry. Its contribution to the PM2.5 is 16 %.

Finally, the secondary aerosol source, that accounts for a 29 % of the total and is associated with $NO_3^-$and NH_4^+. It is interesting to see in Figure 6.14 the temporal variation of this source. As expected, nitrate aerosols present higher contribution in winter than in summer. The reasons for that are favourable conditions for NO_3^- formation during the cold season as low temperature and stable meteorology favour the reaction of ammonia with nitric acid to form ammonium and nitrate (Khan, 2009).

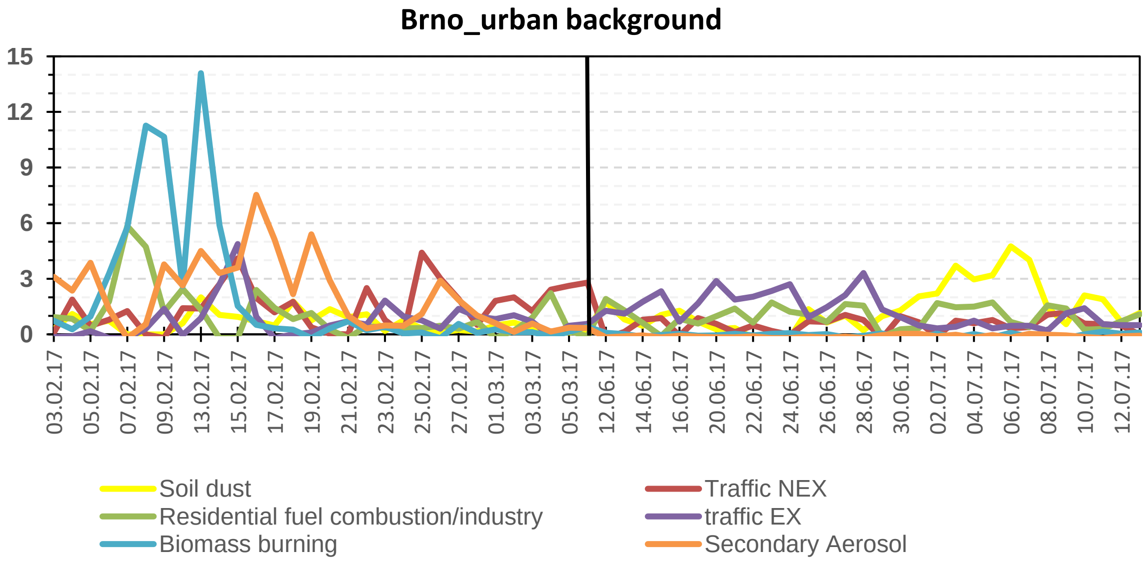


Figure 6.14. Temporal variation of normalized factor contribution for Brno urban background.

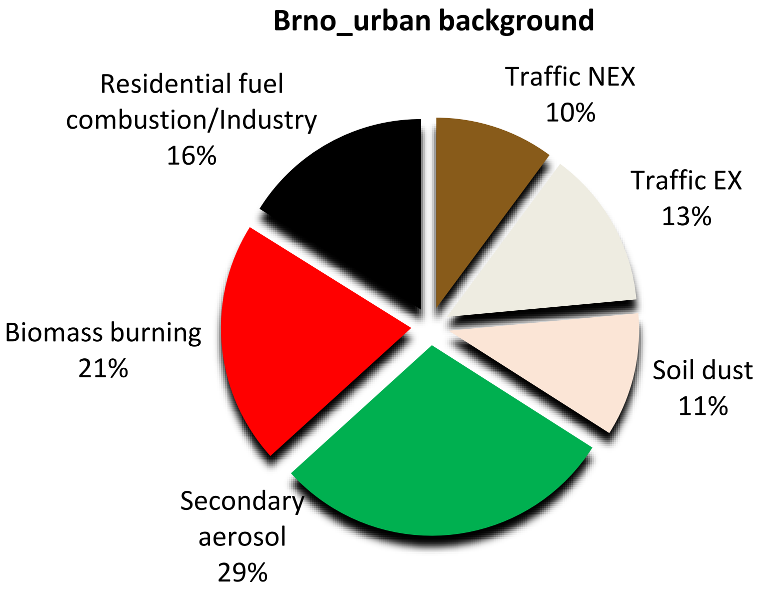


Figure 6.15. Source contribution of the six factors to the measured PM2.5 concentration for the urban background site in Brno in percentage.

6.3.2c Brno traffic site

The results for the species contribution in each source in the traffic site measurement station in Brno can be seen in Figure 6.16. Seven sources have been identified by using 72 samples and 32 species. Constrains for Cl^- and EC have been used under the limitation dQ %< 0,5 for the factor Traffic EX (pull down maximally and pull up maximally, respectively).

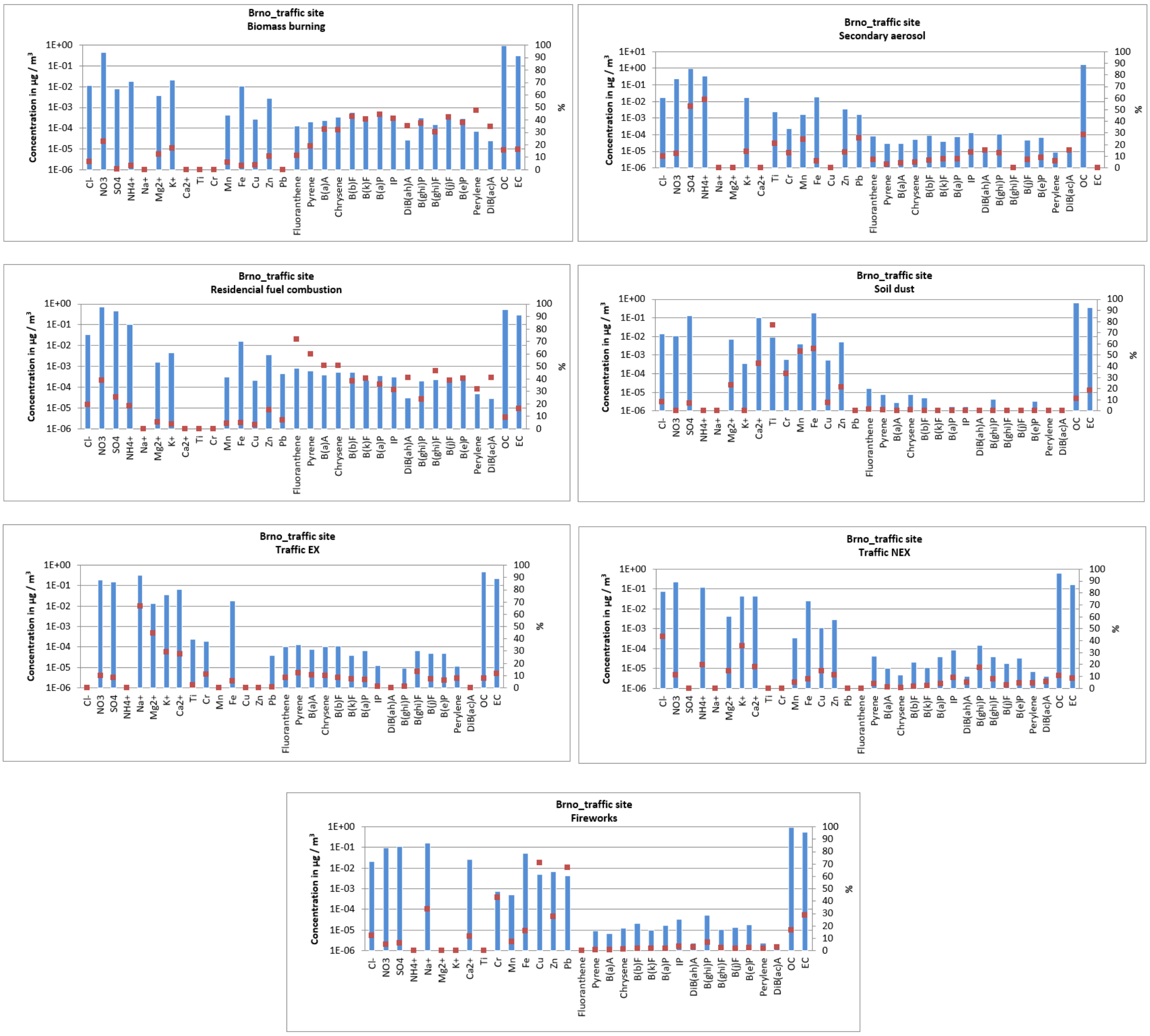


Figure 6.16. Factor profiles in µg m^{-3} and percentage of contribution of the species for the traffic site in Brno.

The biomass burning-related sources are represented by high concentration of K, OC, EC and PAHs. As can be seen in Figure 6.18, biomass burning contributes with 13 % of the total source contribution to PM2.5. However, this contribution is exclusively in winter. As it is shown in Figure 6.17, the temporal contribution of the biomass burning category has its minimum during the summer months.

The second factor is distinguished by high concentrations of SO_4^{2-} and NH_4^+, suggesting that it is a source associated with the formation of secondary sulphate aerosols. It accounts for the 24 % of the total source contribution to the mass of PM2.5.

The third factor identified by PMF is distinguished by high concentrations of PAHs, fluoranthene and pyrene for instance, which are well-known indicators for residential fuel combustion. It contributes to the PM2.5 mass concentration with 17 %.

The fourth factor is distinguished by high concentrations of Ti, Cr, Ca, Mn and Fe and is suggested to be particles emitted from unpaved roads, construction sites, and wind-blown soil dust. It contributes to the PM2.5 mass concentration with 10 %.

The next two factors are related to the traffic. Traffic exhaust (10 % of the PM2.5 mass) has been traced by relatively high concentrations of OC, EC and PAHs. As in the urban background station, high loading for Na^+ has been found. This species could have its origin in the transboundary long-range transport coming from the sea or an anthropogenic source (road salt). The non-exhaust sources category accounts for 11 % of the total source contribution to PM2.5 and it has been traced by Fe, Cu and Zn.

An extra factor has been identified as coming from Fireworks due to presence of a large amount of Pb, Cu and Zn. Potassium is usually the main marker for direct fireworks (Tian Y. Z. , J. Wang J. , Peng X. , ShiG. L. , and Feng Y. C., 2014). However, the PMF model could not distinguish the contribution of K to this category. This source was not clearly identified and, according to the bootstrap error estimation analysis, the sources traffic NEX and Fireworks had interchanged part of their contribution which explains the significant amount of potassium found in the traffic NEX factor and the general contribution to the PM2.5 and the temporal contribution of the fireworks category to the PM2.5 mass concentration which is extremely large (15 %). The firework competition took place from 26/5 to the 24/6/17, which means that the contribution of this source during the rest of the year is coming from the traffic NEX.

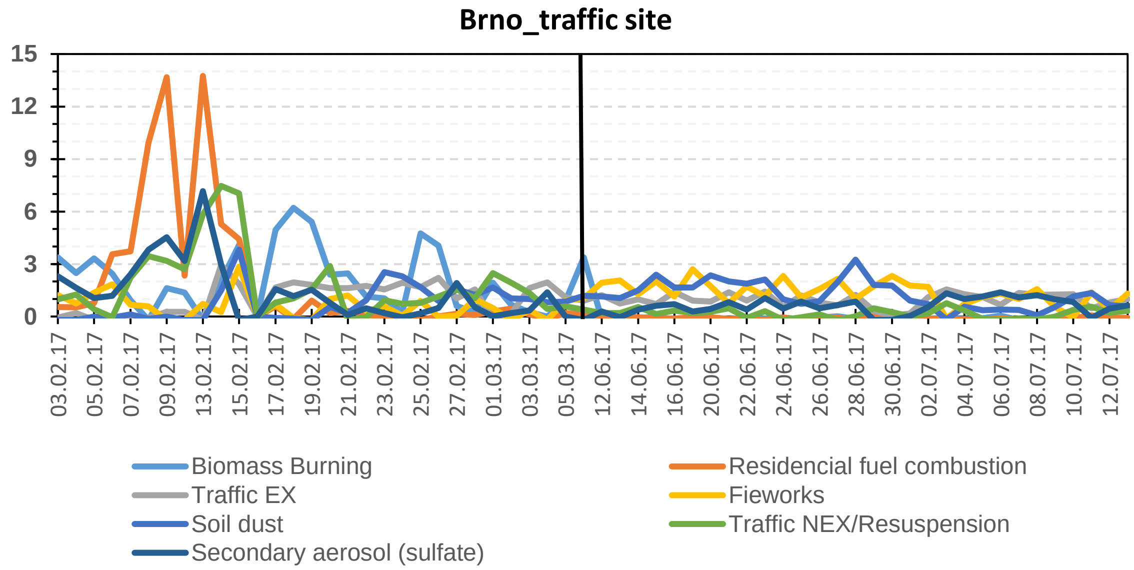


Figure 6.17. Temporal variation of normalized factor contribution for Brno traffic site.

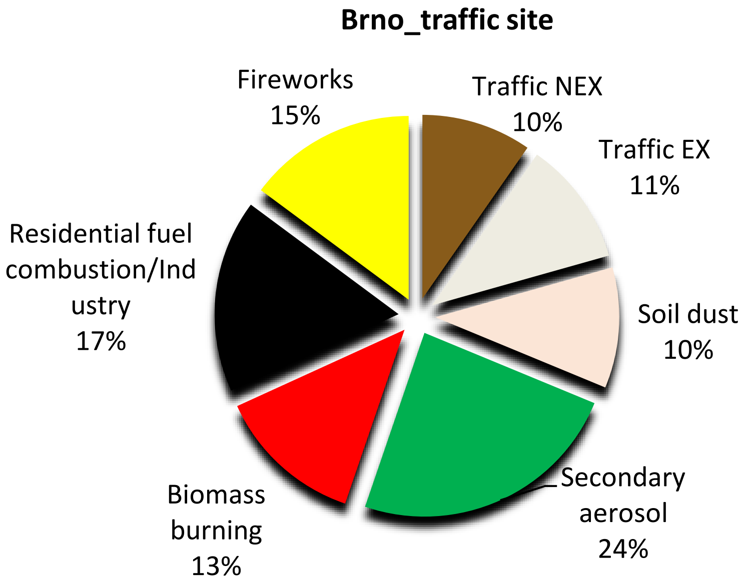


Figure 6.18. Source contribution of the seven factors to the measured PM2.5 concentration for the traffic site in Brno in percentage.

6.3.3 Results for Ljubljana

6.3.3a Ljubljana regional background

The results for the species contribution in each source in the traffic site measurement station in Ljubljana can be seen in Figure 6.19. Seven sources have been identified by using 55 samples and 15 species.

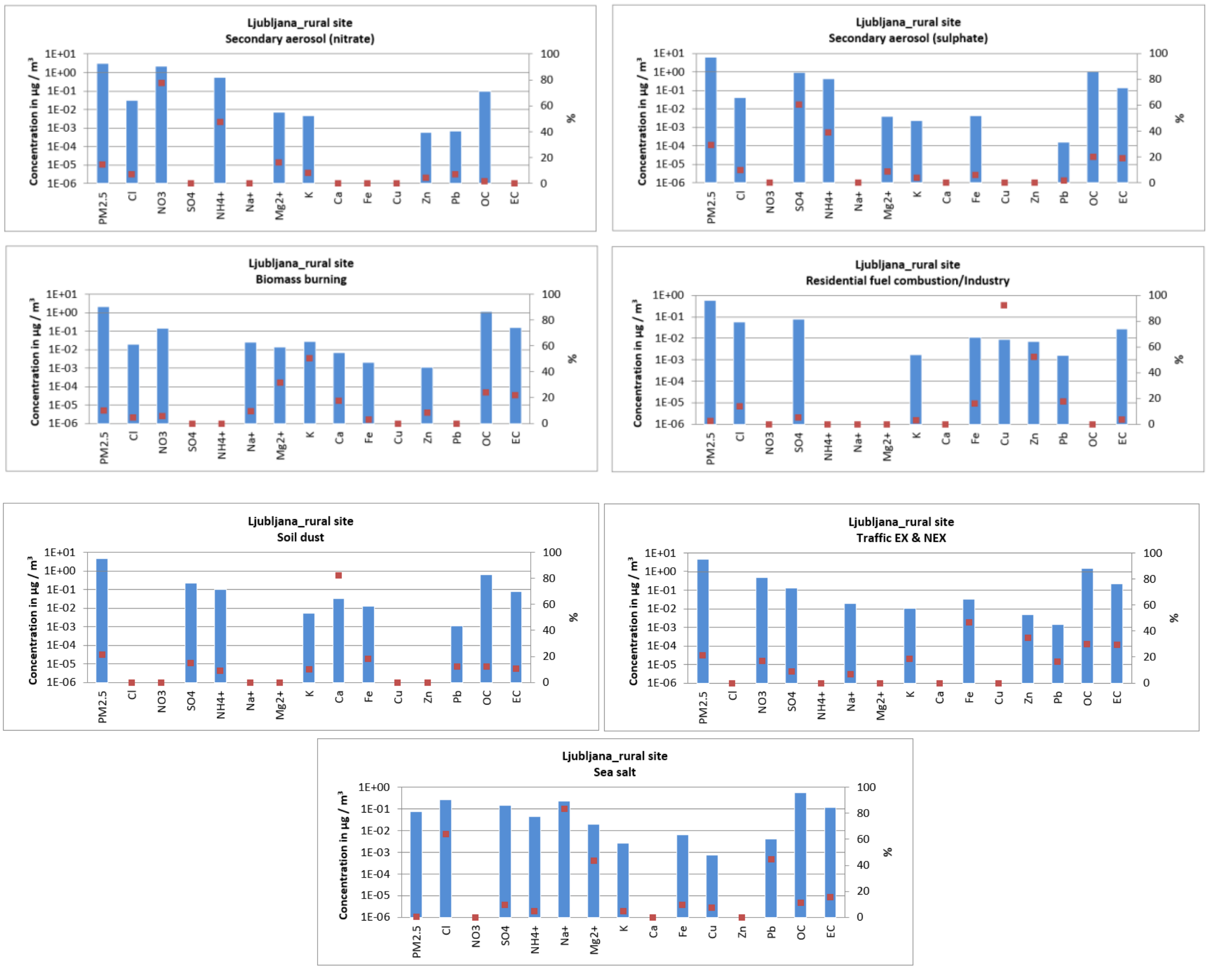


Figure 6.19. Factor profiles in µg m^{-3} and percentage of contribution of the species for the regional background site in Ljubljana.

The first and second factors are distinguished by high concentrations of NO_3^- and SO_4^{2-}, respectively, suggesting that they are sources associated with the formation of secondary nitrate and sulphate aerosols. They account for the 15 % and 29 % of the total source contribution to the mass of PM2.5, respectively. As can be seen in Figure 6.20, only nitrate aerosols source shows seasonal variation.

The third and fourth factors present a significant variation between summer and winter which means that they must both be related with residential heating. The third factor has been identified as biomass burning as it has high loadings for K, OC and EC. The fourth has been categorized as residential fuel combustion / industry, as it presents high loadings for Cu, Zn and Pb.

They account for the 10 % and 3 % of the total source contribution to the mass of PM2.5, respectively.

The fifth factor is distinguished by high concentrations of Ca, Al and Fe and is suggested to be particles emitted from unpaved roads, construction sites, and wind-blown soil dust. It contributes to the PM2.5 mass concentration in a 22 % and it does not present seasonal variation.

One unique factor has been identified with traffic-related species as it is formed by not only high loadings of OC and EC in a 1 to 1 ratio but also Fe, Zn and small amounts of Pb. This source presents peaks in winter but in general in remains stable through the measurement campaigns. The contribution of the traffic-related components to the total PM2.5 mass is 21 %.

A small sea salt contribution (0.35 %) has been also traced by Cl^-, Na^+ and Mg^{2+}.

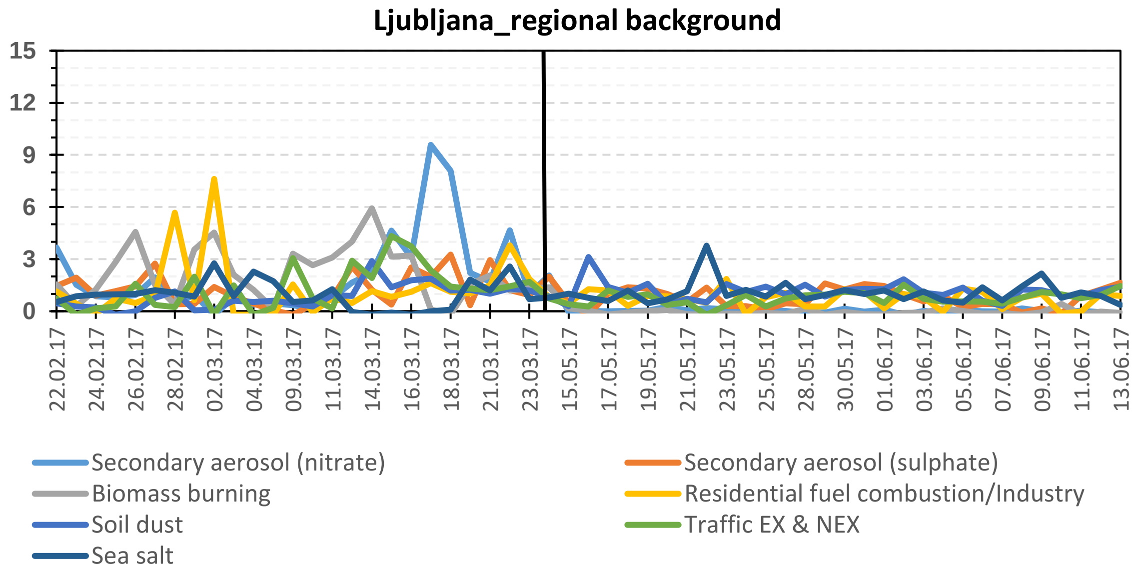


Figure 6.20. Temporal variation of normalized factor contribution for Ljubljana regional background.

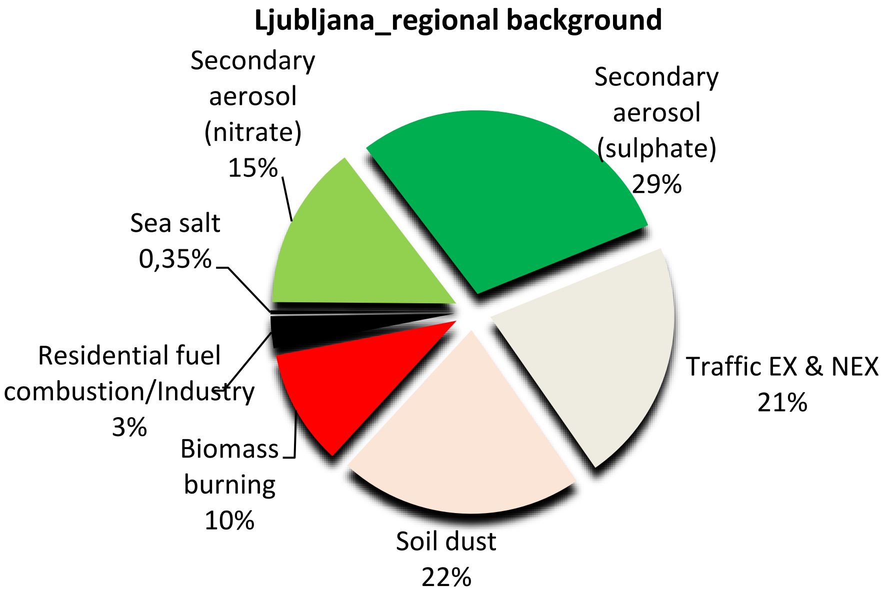
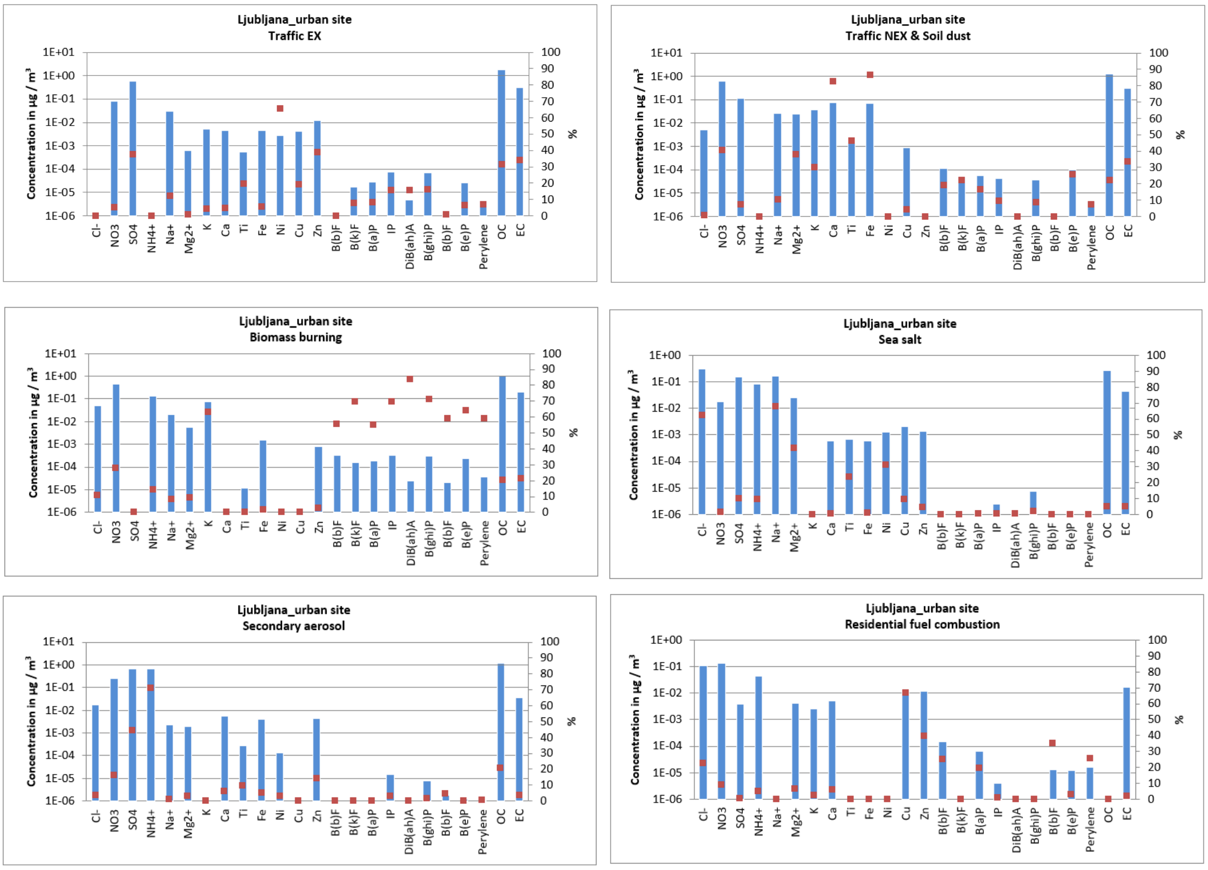


Figure 6.21. Source contribution of the seven factors to the measured PM2.5 concentration for the regional background site in Ljubljana in percentage.

6.3.3b Ljubljana urban background

The results for the species contribution in each source in the traffic site measurement station in Ljubljana can be seen in Figure 6.22. Six sources have been identified by using 58 samples and 24 species.



Ljubljana_urban site Traffic EX

Ljubljana_urban site Traffic NEX & Soil dust

Ljubljana_urban site Biomass burning

Ljubljana_urban site Sea salt

Ljubljana_urban site Secondary aerosol

Ljubljana_urban site Residential fuel combustion

Figure 6.22. Factor profiles in µg m^{-3} and percentage of contribution of the species for the urban background site in Ljubljana.

Traffic exhaust sources have been associated with high loadings for OC and EC at ratio close to 1. Traces of Ni have also been found in this factor. As can be seen in Figure 6.23 and Figure 6.24 it does not show seasonal variation and it is one of the prevailing sources of PM2.5 in this site together with secondary aerosols (24 %).

The second factor presents high loadings for Ca and Fe, as well as OC, EC and PAHs and it presents seasonal variation. The source has been identified as traffic non-exhaust sources and soil dust. However, it could also have components that are coming from the biomass burning and have not been correctly categorized by the PMF model so that the unexpected seasonal variation that this source shows is explained. This factor accounts for the 22 % of the total contribution to the PM2.5 mass.

High loadings for K, OC, EC and PAHs have been associated with biomass burning. This source is only present in winter and has a contribution of 18 % to the total mass of PM2.5.

Sea salt has been traced by Na^+ and Cl^- It is worth mentioning that the contribution of this source in the PM2.5 mass is the highest found in all the participating cities with a 9 %.

A high contribution of NH_4^+ and SO_4^{2-} characterize a secondary sulfate source. It accounts for 24 % of the total mass concentration of PM2.5 and remains stable during both campaign periods although it has more contribution in winter.

Residential fuel combustion has been traced by Cu, Zn and some PAHs. As can be seen in Figure 6.23, it has a clear seasonal variation that rockets in specific days in winter and drops dramatically in summer. It has, however, a small contribution, only representing the 3 % of the total source contribution to the mass of PM2.5.

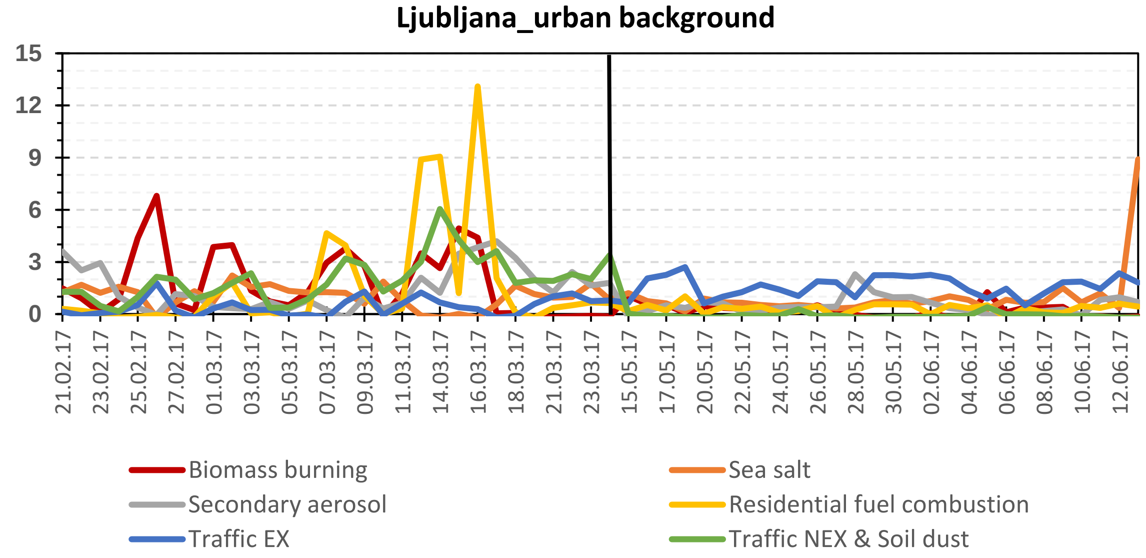


Figure 6.23. Temporal variation of normalized factor contribution for Ljubljana urban background.

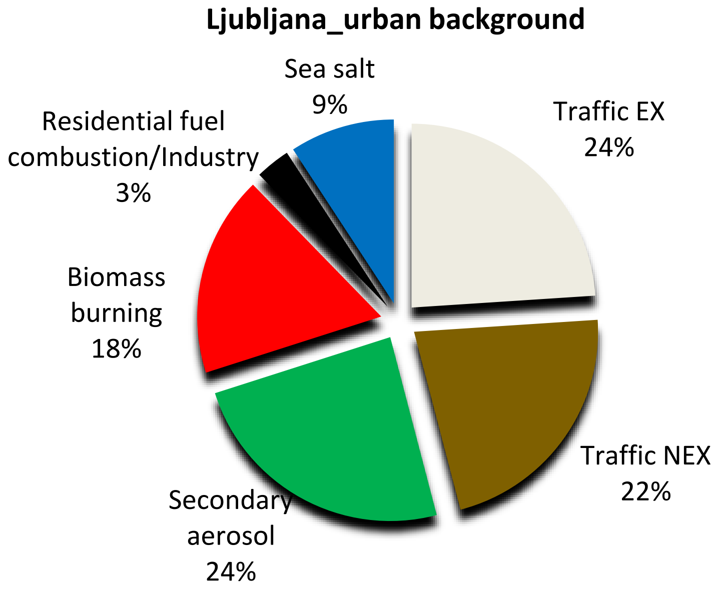


Figure 6.24. Source contribution of the six factors to the measured PM2.5 concentration for the urban background site in Ljubljana in percentage.

6.3.3c Ljubljana traffic site

The results for the species contribution in each source in the traffic site measurement station in Ljubljana can be seen in Figure 6.25. Six sources have been identified by using 55 samples and 27 species.

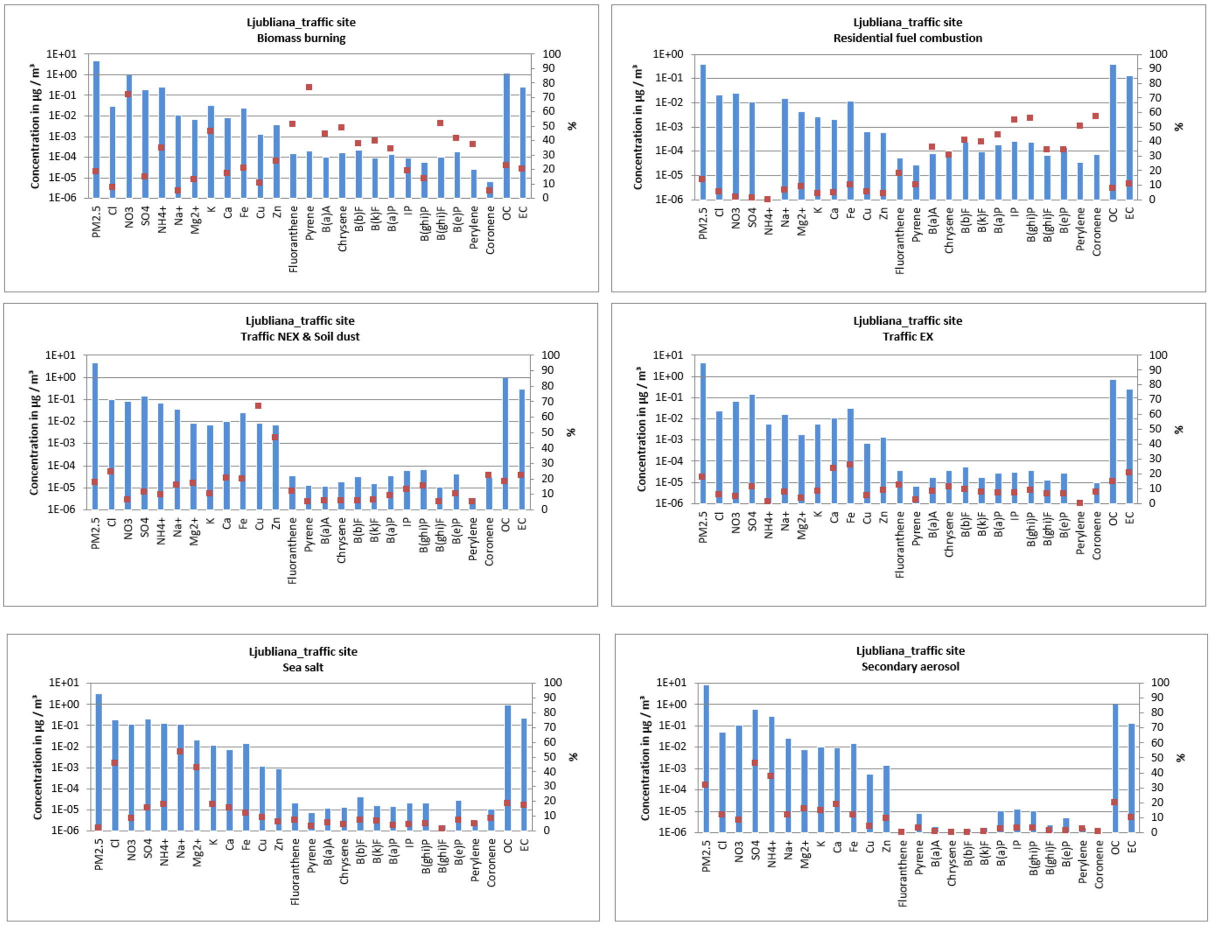


Figure 6.25. Factor profiles in µg m^{-3} and percentage of contribution of the species for the traffic site in Ljubljana.

The first two factors present the special feature of having a clear seasonal variation, as can be seen in Figure 6.26. The first one has been associated with biomass burning as it presents K, OC, EC, pyrene and other heavy PAHs as markers. It also shows a significant amount of NO_3^- and NH_4^+ as nitrate aerosols have the same temporal pattern and the PMF software identifies as one factor the species that present the same temporal trends. Residential fuel combustion has been traced by the PAHs and the carbon compounds. Biomass burning and residential fuel combustion contribute to the total mass of PM2.5 with 18 and 13 %, respectively.

Higher loadings of Cu and Zn denote the presence of traffic non-exhaust sources as a source of PM2.5 in this site. Several peaks appear in its temporal distribution which could indicate that the source is in fact a mix with soil dust and it suffers resuspension due to the wind in some specific days (1/3, 15/3 and 2/6/17, for instance). Its contribution to the total mass of PM2.5 is 18 %.

The traffic exhaust gas has been associated with high concentration OC and EC. It does not present temporal variation and its contribution to the total mass of PM2.5 is 18 %.

The prevailing source is secondary aerosols, mainly formed by sulphate aerosol and OC. It does not present temporal variation and accounts for 31 % of the total PM2.5 mass. A small contribution of sea salt (2 %) traced by Cl^- and Na^+ can also be observed.

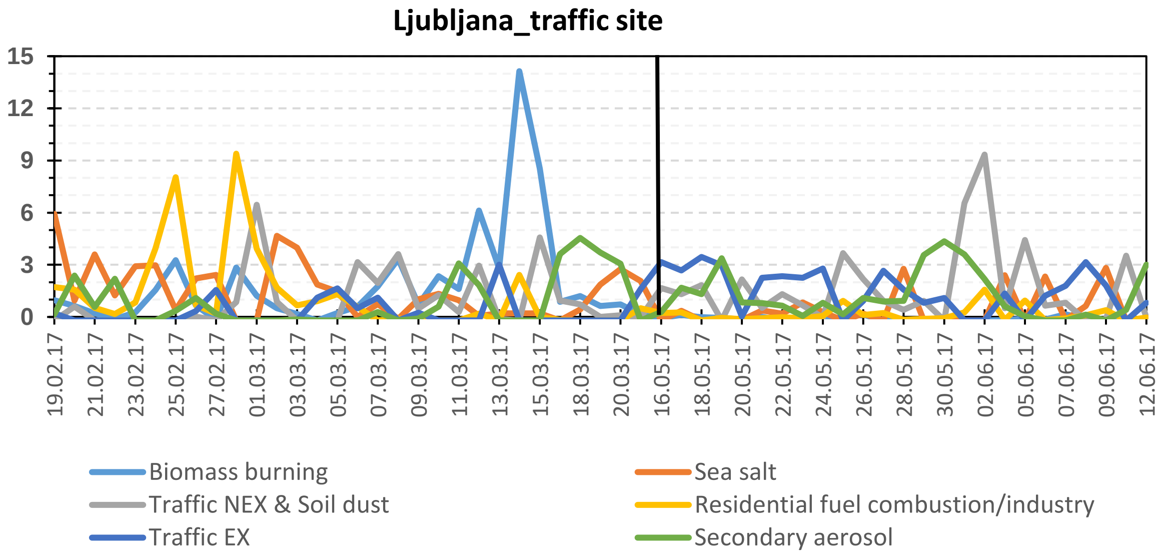


Figure 6.26. Temporal variation of normalized factor contribution for Ljubljana traffic site.

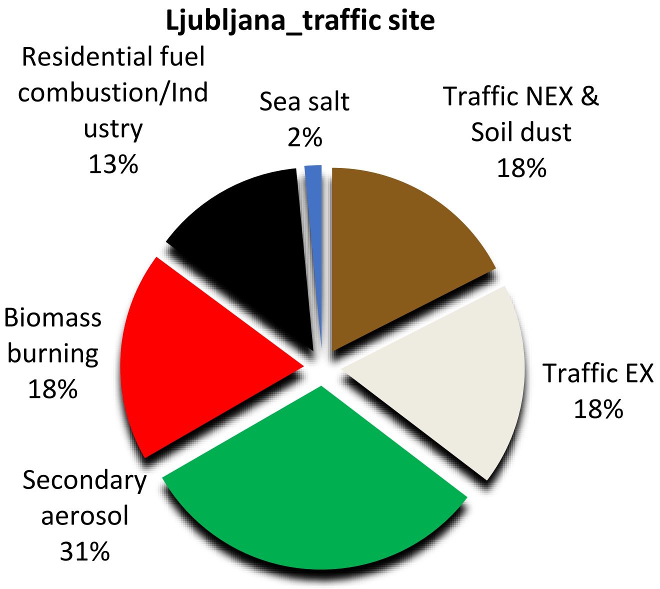


Figure 6.27. Source contribution of the six factors to the measured PM2.5 concentration for the traffic site in Ljubljana in percentage.

6.3.4 Results for Madrid

6.3.4a Madrid regional background

The results for the species contribution in each source in the regional background measurement station in Madrid can be seen in Figure 6.28. Six sources have been identified by using 55 samples and 16 species. Constrains for OC and EC have been used under the limitation dQ %< 0,5 for the factor biomass burning (pull down maximally).

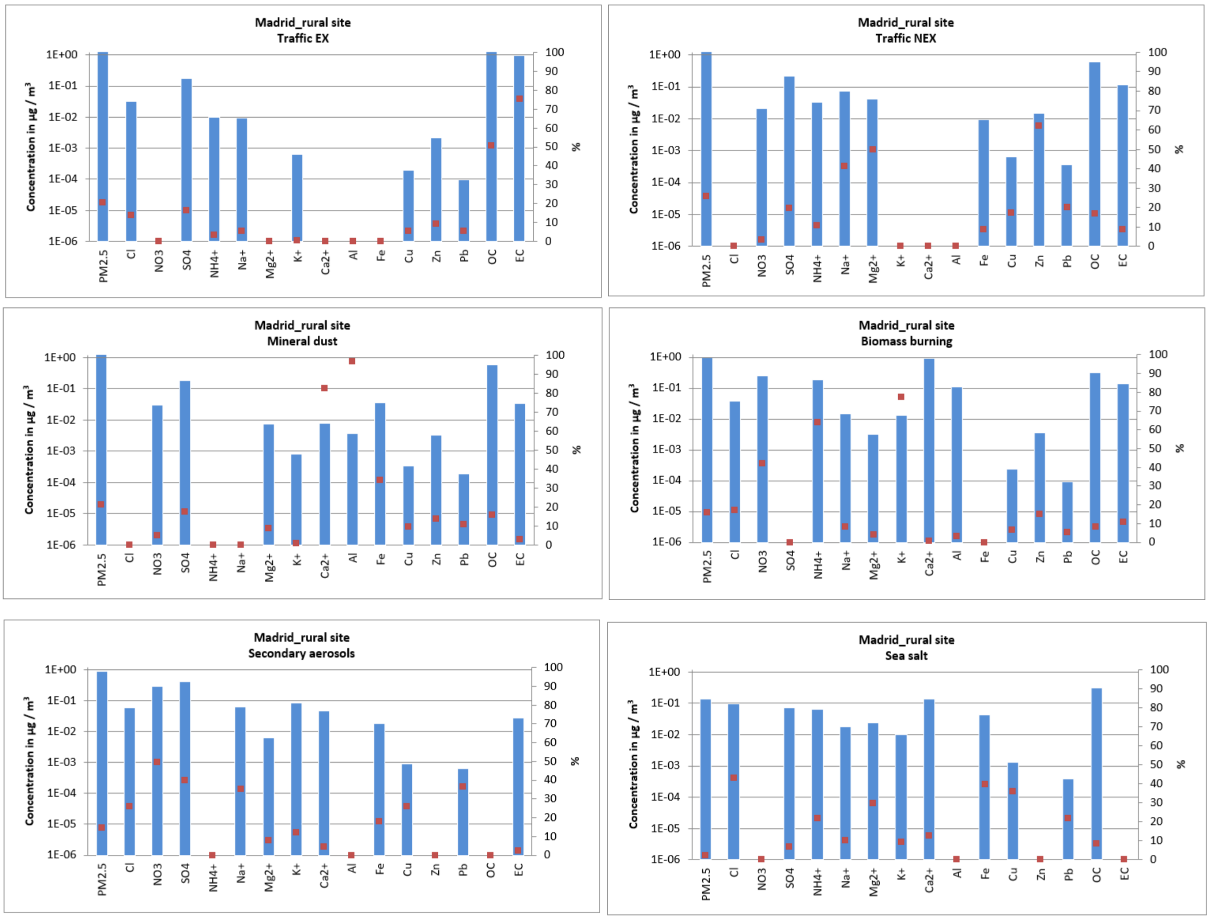


Figure 6.28. Factor profiles in µg m^{-3} and percentage of contribution of the species for the regional background site in Madrid.

The first two factors are related to the traffic. Traffic exhaust (20 % of the PM2.5 mass) has been traced by high concentrations of OC and EC. The non-exhaust sources category accounts for 21 % of the total source contribution to PM2.5 and it has been traced by Cu and Zn. As happened in Brno in the traffic station, high loading for Na^+ has been found, together with Mg^{2+}. These two species could indicate the presence of aged salt, which could be caused by long range transport, or have an anthropogenic source. The non-exhaust traffic source accounts for 26 % of the total source contribution to the mass of PM2.5. As can be seen in Figure 6.29, neither of the traffic categories present seasonal variation.

The third factor is distinguished by high concentrations of Ca, Al and Fe and is suggested to be particles emitted from unpaved roads, construction sites, and wind-blown soil dust. It contributes to the PM2.5 mass concentration with 21 %. It is interesting to see, that this factor has been traced by a 97 % of Al. This high percentage can be explained by the soil composition of the Casa de Campo park, where the measurement station is located, which is mainly clay composed by aluminosilicates ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$).

The fourth factor has been associated with biomass burning as it presents K^+ as tracer. As can be seen in Figure 6.29, it is the only factor that presents seasonal variation, being its contribution of 16 %.

The fifth factor is distinguished by high concentrations of $SO_4^{2-}$and NO_3^-, suggesting that it is a source associated with the formation of secondary sulphate and nitrate aerosols. It accounts for 15 % of the total source contribution to the mass of PM2.5.

A small sea salt contribution (2 %) has been also traced by Cl^- and Mg^{2+}.

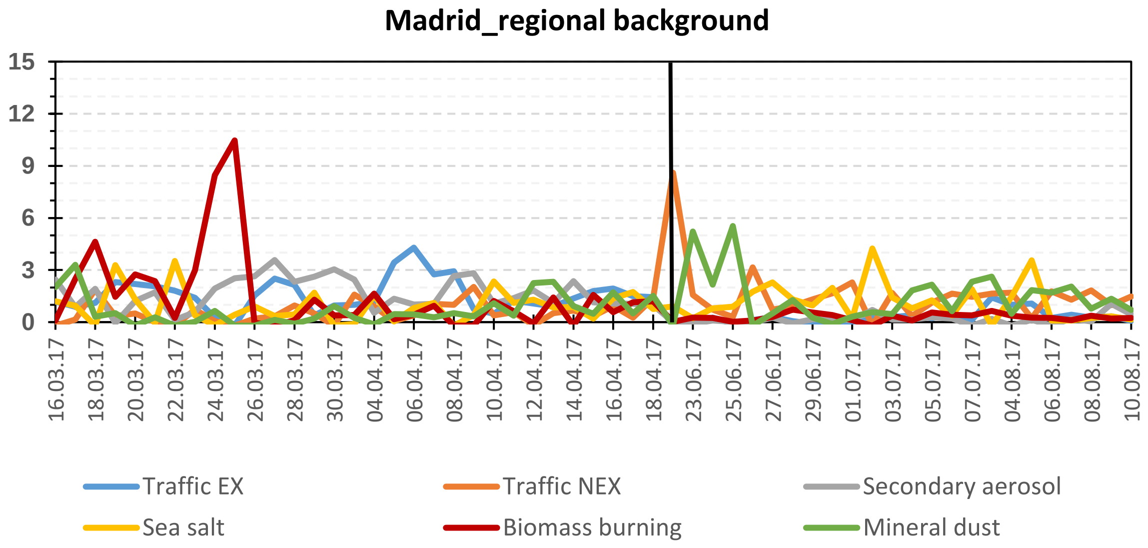


Figure 6.29. Temporal variation of normalized factor contribution for Madrid regional background site.

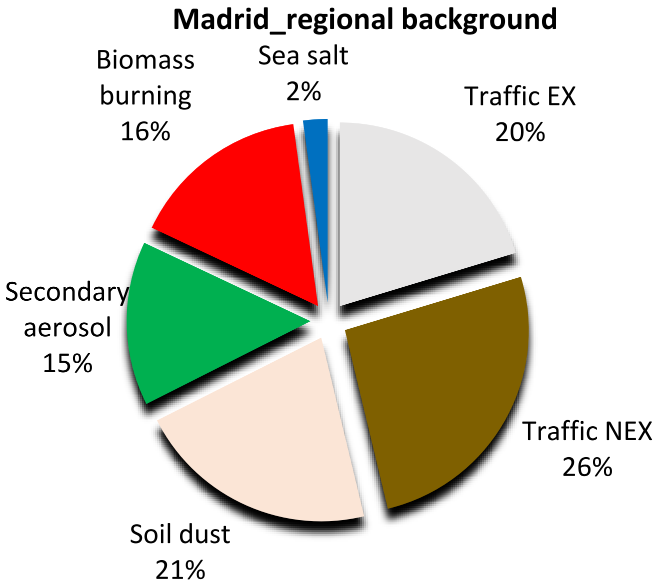


Figure 6.30. Source contribution of the six factors to the measured PM2.5 concentration for the regional background site in Madrid in percentage.

6.3.4b Madrid urban background

The results for the species contribution in each source in the urban background measurement station in Madrid can be seen in Figure 6.31. Six sources have been identified by using 62 samples and 23 species.

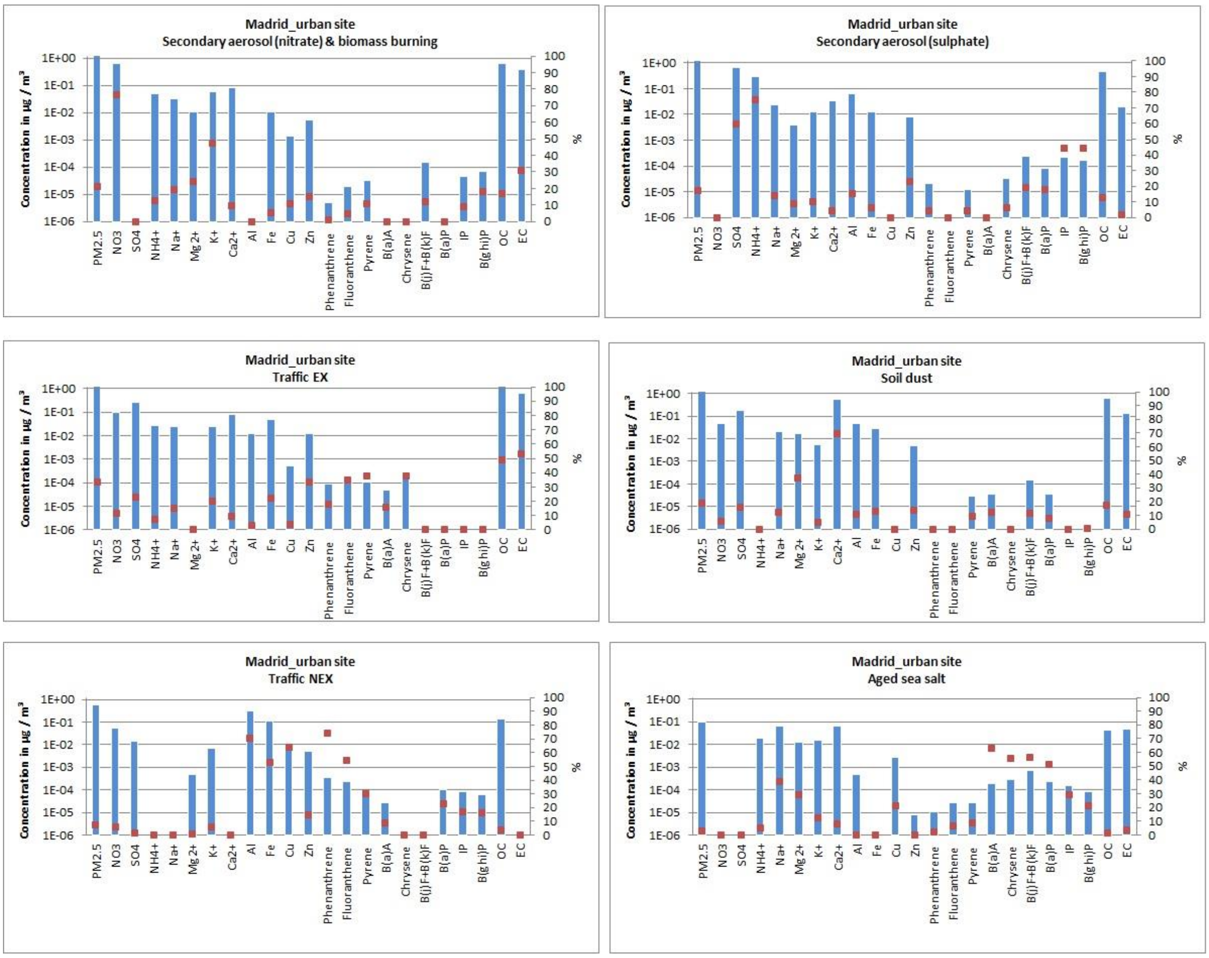


Figure 6.31. Factor profiles in µg m^{-3} and percentage of contribution of the species for the urban background site in Madrid.

The first factor has been associated with two sources, on the one side, secondary nitrate and on the other side biomass burning traced by high loadings for K$^+$, OC and EC. These sources present the same temporal pattern (higher in winter than in summer) so the model cannot differentiate them properly. The contribution of this factor to the total mass of PM2.5 is 21 %.

A high contribution of NH_4^+ and SO_4^{2-} characterizes a secondary sulfate source. It accounts for 17 % of the total mass concentration of PM2.5 and remains stable during both campaigns (no seasonal variation).

High loadings for OC and EC has been used to identify the source traffic exhaust. The contribution of this source to the PM2.5 is one of the highest found compared to other cities and stations, that is 33 %. As can be seen in Figure 6.32, it does not present seasonal variation.

The soil dust source is distinguished by high concentrations of Ca^{2+}. This source presents more peaks in summer than in winter and contributes to the PM2.5 with 19 %.

The source non-exhaust traffic emissions has been associated with high loadings for Al, Fe, Cu and some PAHs (phenanthrene and fluoranthene). Al and Fe, which are mineral dust, are in fact coming from the resuspension of the soil particles and Cu is associated with brake wear. This source does not present seasonal variation. However, five peaks along the measurement campaigns can be observed in Figure 6.32. The contribution of this source to the PM2.5 mass is 7 %.

A last factor that contributes with 3 % to the PM2.5 mass has been identified as aged salt as it is composed mainly by Na^{+} and Mg^{2+}.

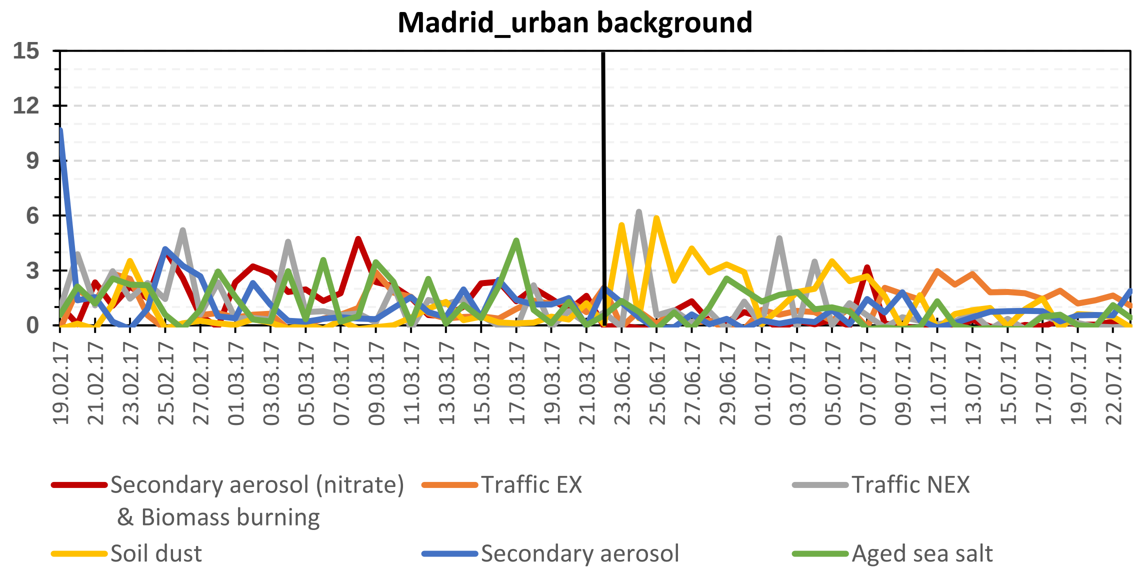


Figure 6.32. Temporal variation of normalized factor contribution for Madrid urban background site.

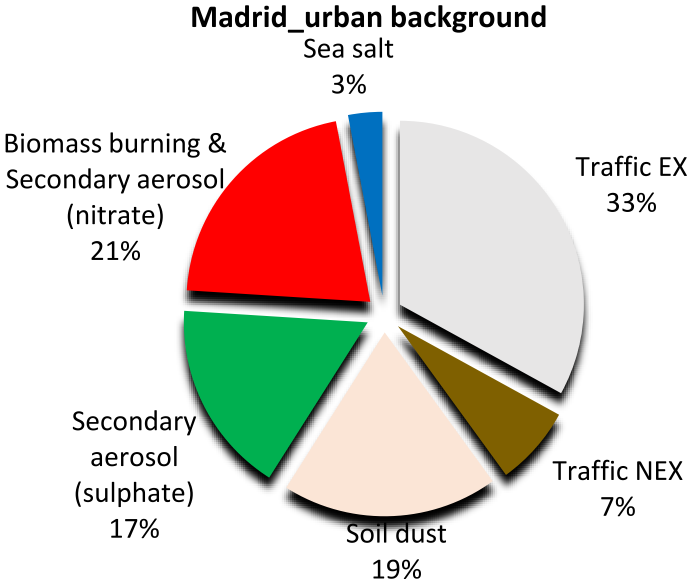


Figure 6.33. Source contribution of the six factors to the measured PM2.5 concentration for the urban background site in Madrid in percentage.

6.3.4c Madrid traffic site

The results for the species contribution in each source in the traffic site measurement station in Madrid can be seen in Figure 6.34. Six sources have been identified by using 62 samples and 21 species. Constrains for two factors have been used, namely for Cu in the source traffic NEX (pull up maximally) and for K in the source residential heating/industry (pull up maximally).

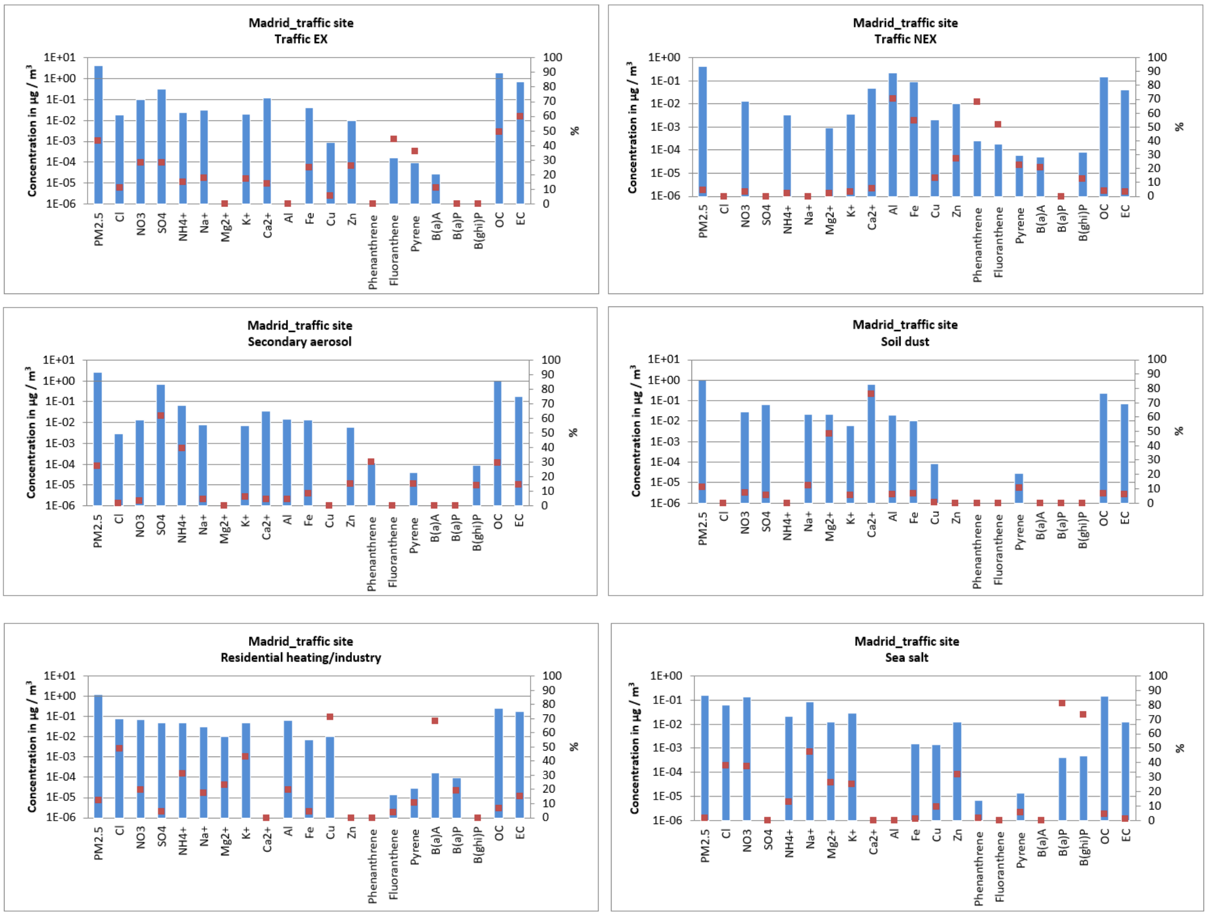


Figure 6.34. Factor profiles in µg m^{-3} and percentage of contribution of the species for the traffic site in Madrid.

As happened in the regional and the urban background station, traffic is the prevailing source, with 47 % of the total contribution to the PM 2.5 mass concentration (see Figure 6.36). From this 47 %, 43 % comes from exhaust sources and 4 % from non-exhaust sources. The traffic exhaust sources have been traced by high loadings for OC and EC and some of the PAHs, specifically fluoranthene and pyrene, which are polyaromatic hydrocarbon with relatively low molecular weight that are characteristic of diesel emissions (Bari A. , 2009). The non-exhaust traffic source has been associated with Al, Fe and relatively light PAHs. These species are coming from the resuspension caused by the traffic. As can be seen in Figure 6.35, traffic related sources do not present season variation. However, peaks appearing in the urban background are observed for non-exhaust traffic emissions.

Factor 3 correlates strongly with NH_4^+ and SO_4^{2-}, consistent with source categories related to secondary particles (secondary sulfate). It includes a considerably high amount of OC, which is also considered to be secondary OC. It is presented as the second largest contribution to the PM 2.5 mass, with 27 %, as can be seen in Figure 6.36.

Soil dust have been identified by traces of Ca. As it is shown in Figure 6.35, dust events are present mainly in summer. The contribution to the PM2.5 mass is 11 %.

Although the use of biomass has not been reported for domestic heating, a significant amount of K has been found along with benzo(a)anthracene, a PAH that is emitted mainly during oil burning. Copper has been also found in this factor which could have been emitted by industry. This category is the only one that presents a clear seasonal variation and contributes with 13 % to the total amount of PM2.5.

Sea salt has been traced by Cl^- and Na^+ and represents a 2 % of the sources of PM2.5 in this station.

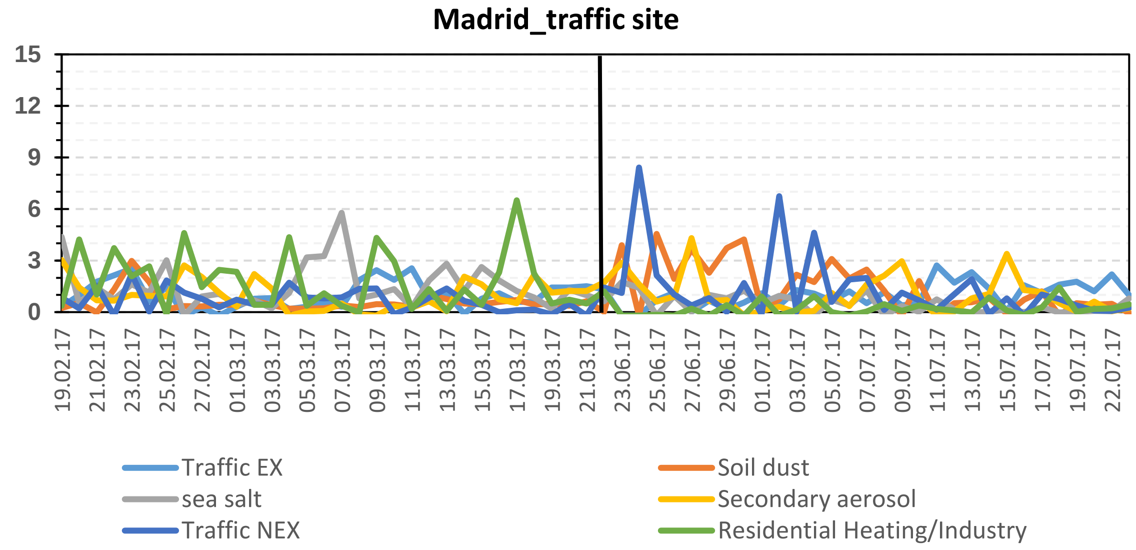


Figure 6.35. Temporal variation of normalized factor contribution for Madrid traffic site.

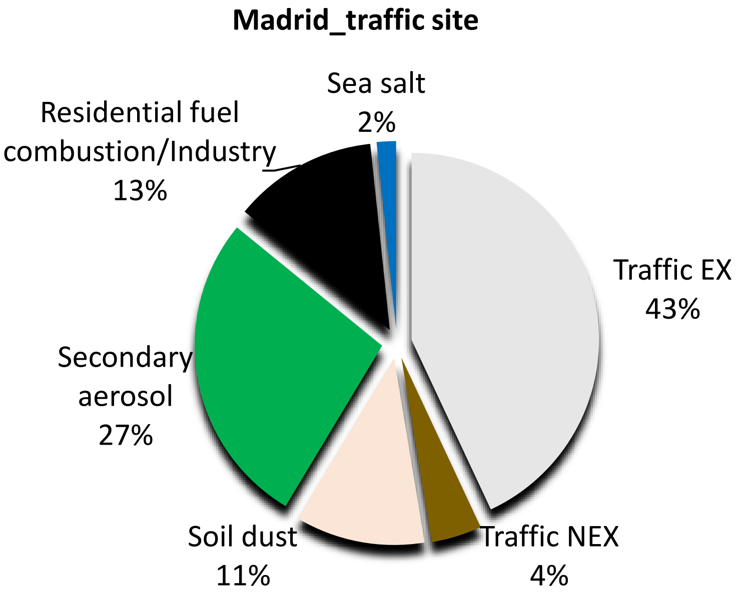


Figure 6.36. Source contribution of the six factors to the measured PM2.5 concentration for the traffic site in Madrid in percentage.

6.3.5 Results for Thessaloniki

6.3.5a Thessaloniki regional background

The results for the species contribution in each source in the regional background measurement station in Thessaloniki can be seen in Figure 6.34. Five sources have been identified by using 60 samples and 27 species.

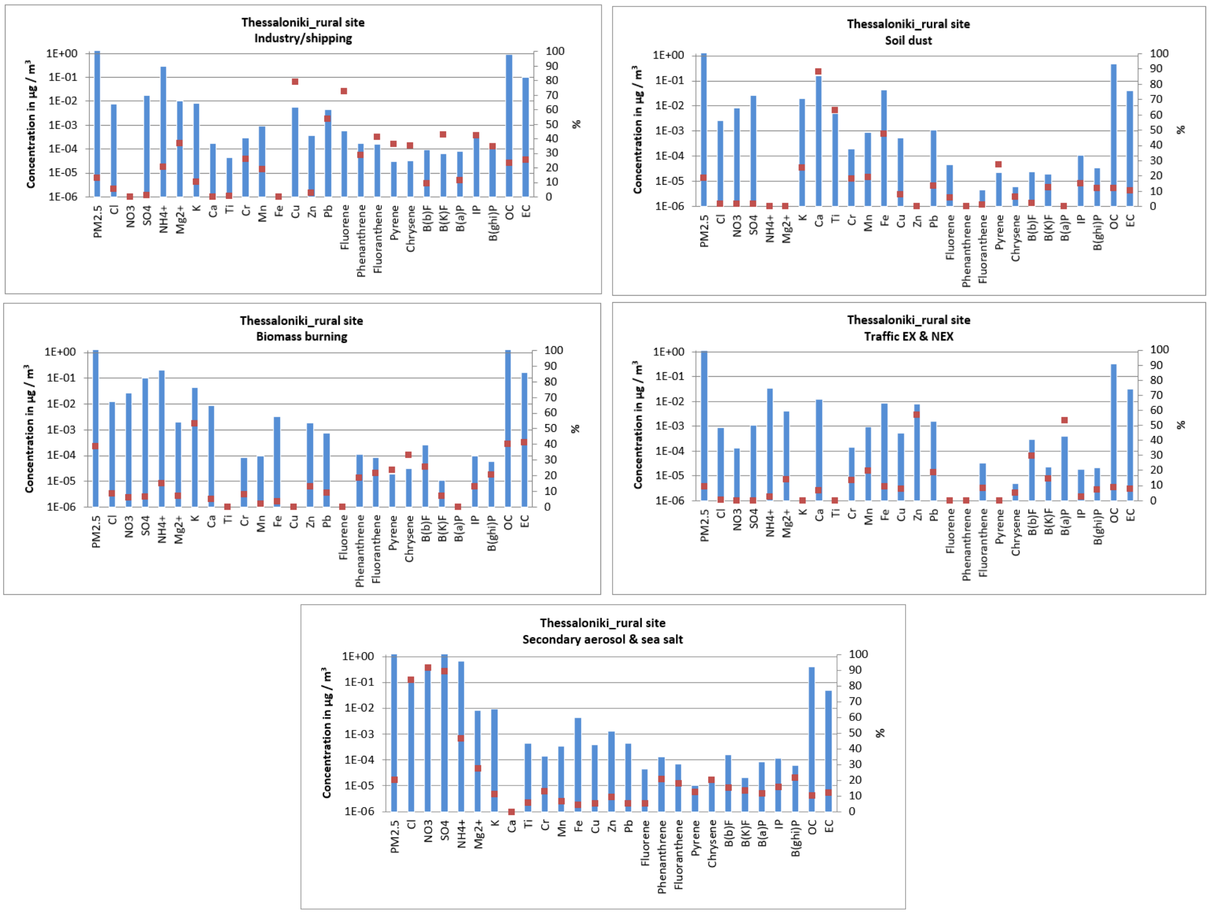


Figure 6.37. Factor profiles in µg m^{-3} and percentage of contribution of the species for the regional background site in Thessaloniki.

The first factor shows high loadings for Cu, Pb, PAHs, OC and EC. It has been associated with industry and shipping as seasonal variation has not been observed and there is an industrial area close to the measurement station (6 km). The contribution of this source is 13 % to the total mass of PM2.5, as shown in Figure 6.39.

The second factor has been traced by Ca, Ti and Fe which are elements coming from the soil dust. It does not present seasonal variation and only one peak on the 30/06/17 is observed corresponding with a dust event. The contribution of soil dust to the total mass of PM2.5 is 19 %.

The highest contribution to the mass of PM2.5 (39 %) in the regional background station in Thessaloniki has been associated with biomass burning as it presents traced of K, OC, EC, PAHs and it is predominant during the cold months mainly. However it is also present in summer which indicates that the biomass burning could come not only from residential heating but also from agricultural burning, which explains the relatively high contribution of agriculture in this site calculated by using the Lenschow approach.

One traffic related source has been distinguished that shows traces of both exhaust sources such as OC, EC and PAHs and non-exhaust sources, namely Zn, an element that is produced by tyre abrasion. The contribution of the traffic to the PM2.5 mass concentration is 9 %, as it is shown in Figure 6.38. It does not present seasonal variation although peaks in summer are observed.

A source containing high loadings for Cl, SO_4^{2-}, NO_3^- and Mg^{2+} have been associated with secondary aerosols and sea salt. It contributes for 20 % of the PM2.5 and due to the nitrates, seasonal variation can be observed.

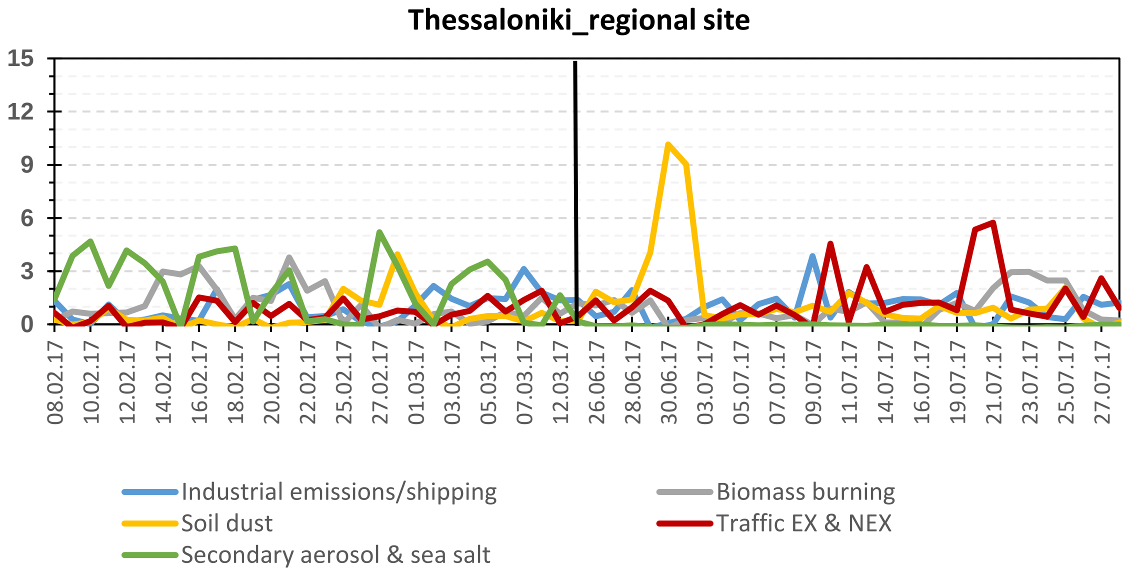


Figure 6.38. Temporal variation of normalized factor contribution for Thessaloniki regional background.

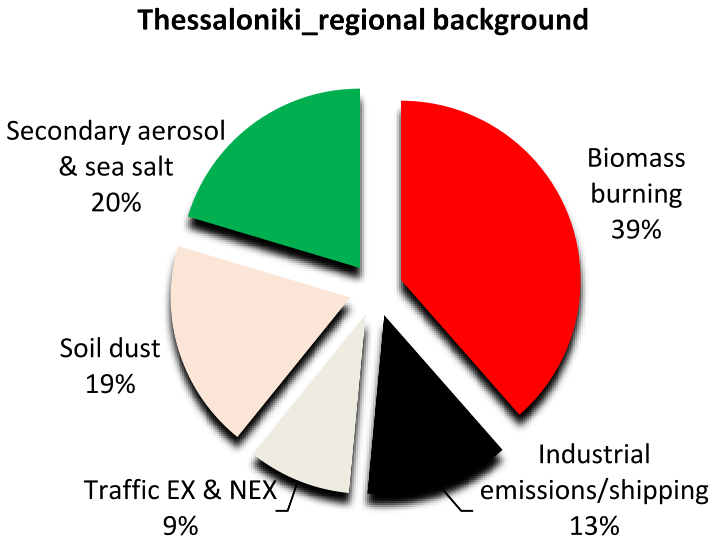


Figure 6.39. Source contribution of the five factors to the measured PM2.5 concentration for the regional background in Thessaloniki in percentage.

6.3.5b Thessaloniki urban background

The results for the species contribution in each source in the urban background measurement station in Thessaloniki can be seen in Figure 6.40. Seven sources have been identified by using 62 samples and 28 species.

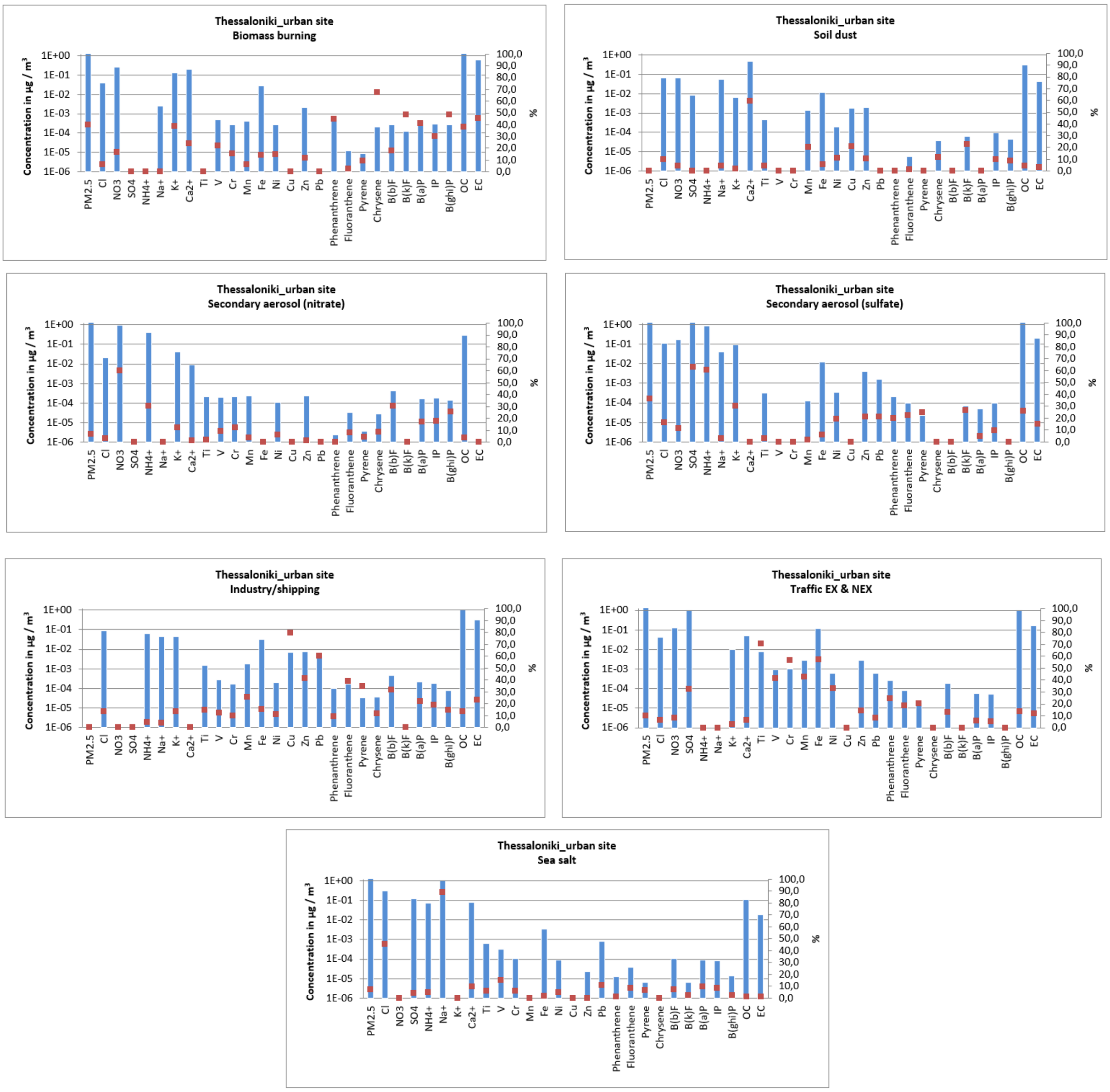


Figure 6.40. Factor profiles in μg m^{-3} and percentage of contribution of the species for the urban background site in Thessaloniki.

The first factor has been distinguished by high loadings for K, OC, EC and PAHs. As can be seen in Figure 6.41, this source is only present during the cold months and represents the second prevailing source of PM2.5 in this site, 32 %.

Soil dust has been traced by high loadings for Ca^{2+}. The contribution of this source to the PM2.5 mass is 3 % in this site. Events where there was intense dust resuspension can be seen in Figure 6.41.

Secondary sulphate aerosol comprises the more abundant source (33 %) of PM2.5, traced by SO_4^{2-} and NH_4^+. Nitrate aerosols has been distinguished as a separate factor traced by NO_3^- and NH_4^+. Its presence is mainly in summer and contributes for 8 %of the mass of PM2.5.

Industrial and shipping emissions have a contribution of 4 % to the PM2.5 mass. Key elements to detect this source have been high loadings of Pb, Zn and Cu and the presence of OC, EC and PAHs. The temporal distribution of this source remains stable during the whole measurement campaign, as shown in Figure 6.41.

The last factor has been distinguished by high loadings for Cl and Na. It accounts for 8 % of the source contribution to PM2.5 and its contribution is more predominant in summer than in winter.

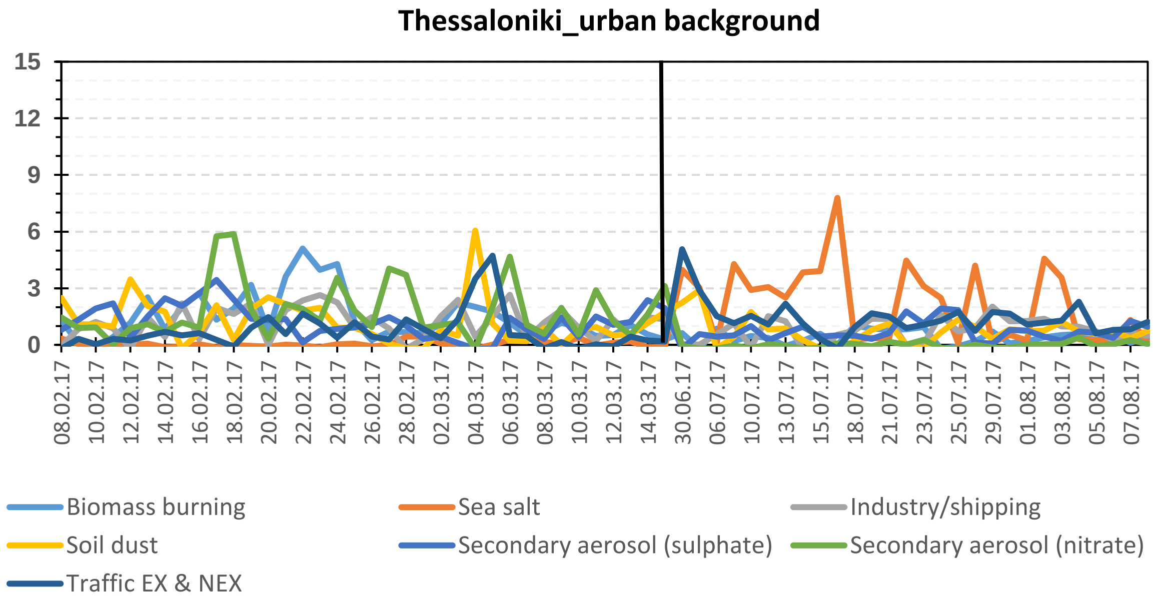


Figure 6.41. Temporal variation of normalized factor contribution for Thessaloniki urban background.

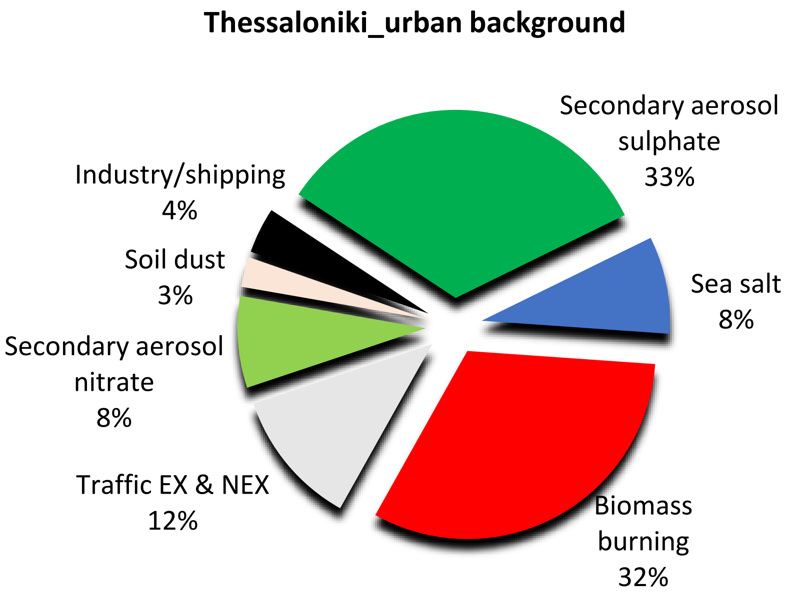


Figure 6.42. Source contribution of the seven factors to the measured PM2.5 concentration for the urban background in Thessaloniki in percentage.

6.3.5c Thessaloniki traffic site

The results for the species contribution in each source in the urban background measurement station in Thessaloniki can be seen in Figure 6.43Figure 6.34. Seven sources have been identified by using 67 samples and 21 species. Constrains for Cl and SO_4^{2-} have been used under the limitation dQ %< 0,5 for the factor Traffic EX (both species pull down maximally) and the factor sea salt and secondary aerosol (pull up maximally for Cl and SO_4^{2-}, respectively).

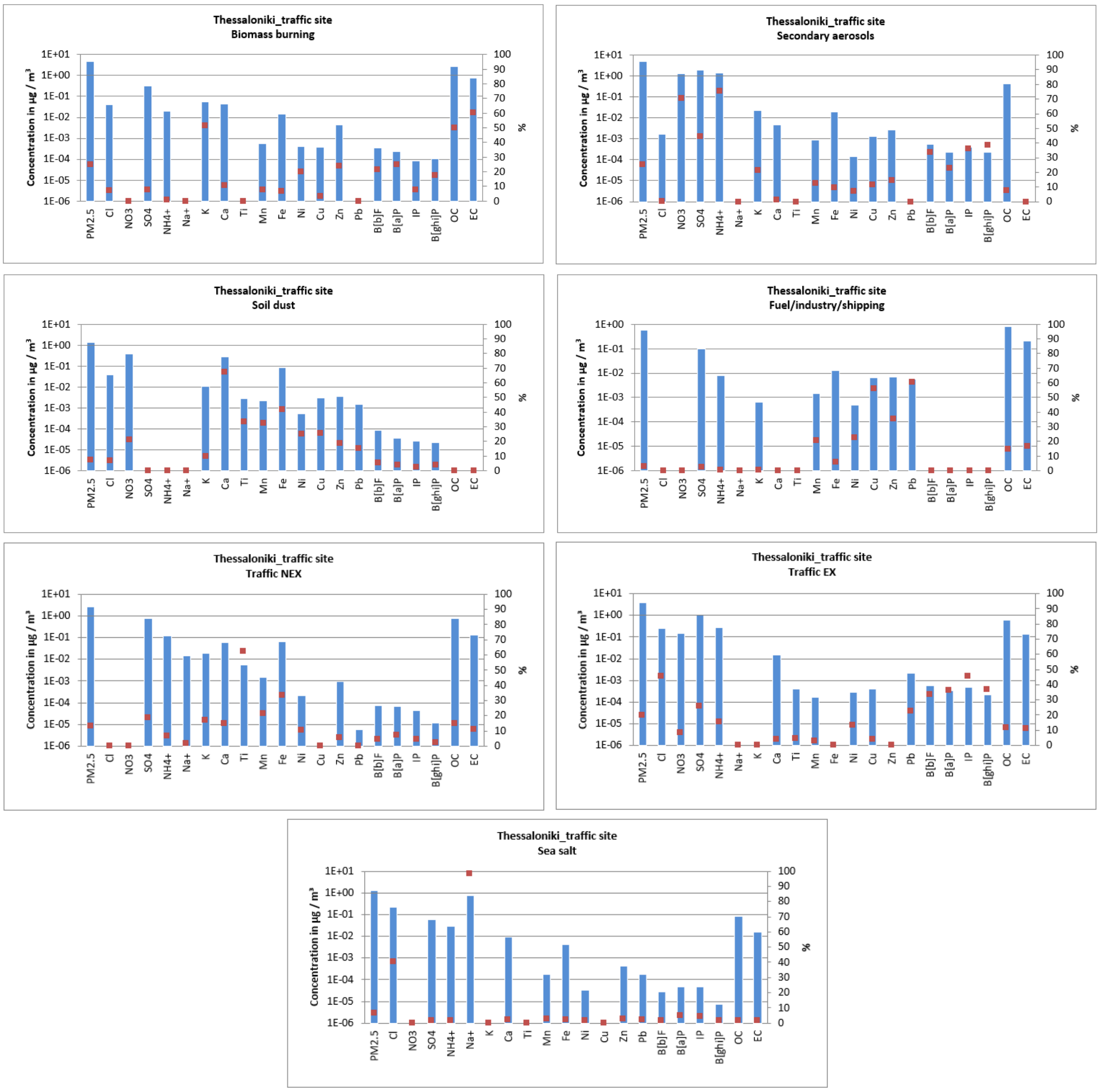


Figure 6.43. Factor profiles in µg m^{-3} and percentage of contribution of the species for the traffic site in Thessaloniki.

As can be seen in Figure 6.43, the first factor presents high loadings for K and carbonaceous species which might indicate biomass combustion as the source category. The seasonal variation of this source can be clearly identified in Figure 6.44. This source represents 25 % of the total source contribution to PM2.5, as can be seen in Figure 6.45.

The second factor correlates strongly with NO_3^- , SO_4^{2-} and NH_4^+ consistent with source categories related to secondary particles (secondary sulfate and secondary nitrate). It presents the highest contribution as a source of PM 2.5, 25 %, together with the biomass burning. This source is predominant in winter than in summer due to the favourable conditions for NO_3^- formation during the cold season as low temperature and stable meteorology favour the reaction of ammonia with nitric acid to form ammonium and nitrate (Khan, 2009).

The third factor corresponds to the source soil dust. This source has been traced by high loading for Ca^{2+}, Ti, Mn and Fe and it accounts for 7 % of the PM2.5 mass. Regarding the temporal distribution of this source, peaks are present during the cold months corresponding with dust events in the city that are also observed in the urban background station.

The fourth factor has been traced by high loadings for Cu, Zn and Pb, the same elements that were found forming a factor in the urban background site. This factor has been associated with industrial and shipping emissions coming from the industrial area and the port (8 and 5 km away from the measurement station, respectively. The contribution of this source to the PM2.5 mass is 3 % slightly lower than in the urban background.

The fifth factor exhibits high loading for Ti and Fe, which can be associated with traffic non-exhaust sources due to the resuspension caused by vehicles. The contribution of the traffic exhaust to the PM2.5 mass in the urban background is 13 %. The pollution coming from the exhaust sources haven been traced by an OC/ EC ratio of 1 and the presence of PAHs. It accounts for 20 % to the PM2.5 mass. No seasonal variation is shown in for the traffic related sources although some peaks are observed for the non-exhaust sources.

A sea salt source has been distinguished by high loadings of Cl^- and Na^+. It accounts for 9 % and shows peaks in summer, as it was observed in the urban background station.

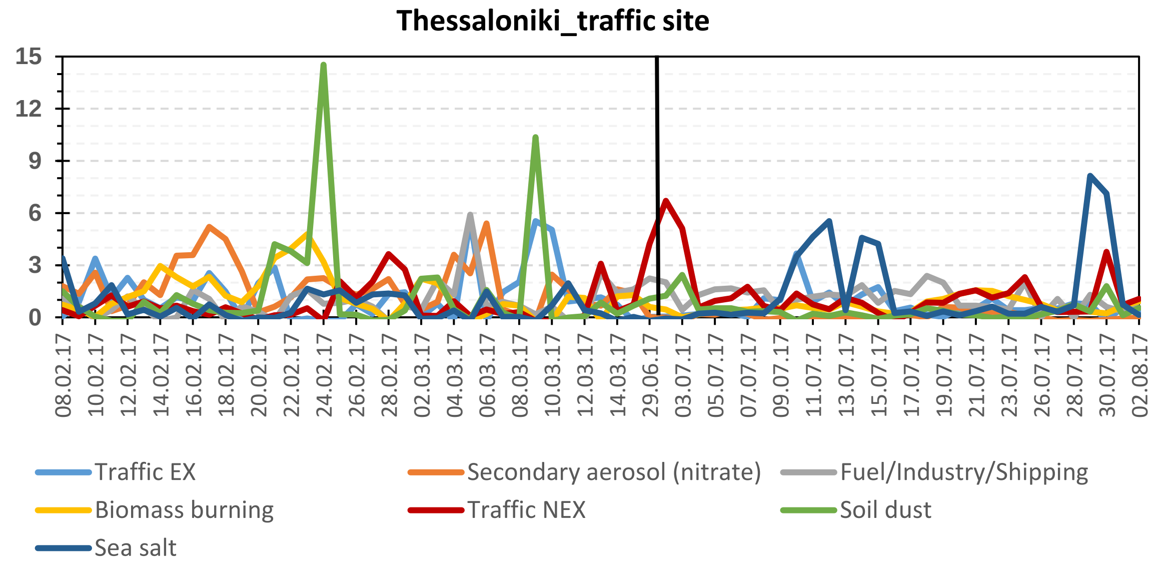


Figure 6.44. Temporal variation of normalized factor contribution for Thessaloniki traffic site.

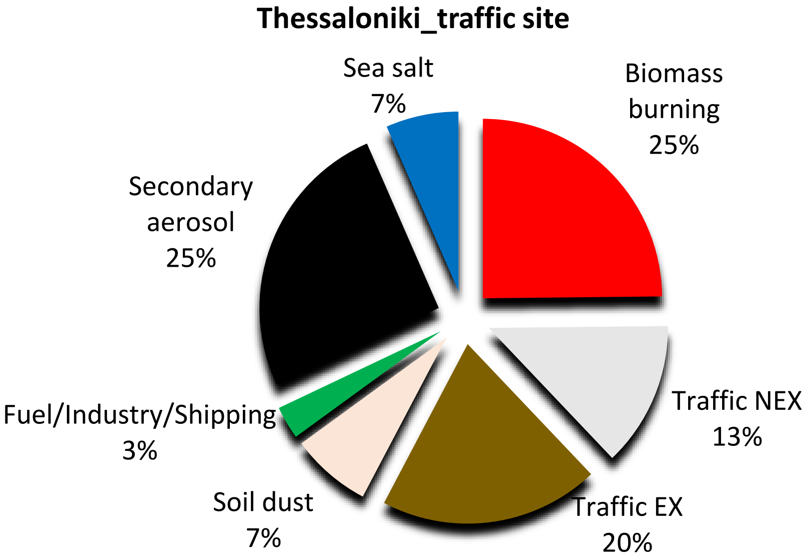


Figure 6.45. Source contribution of the seven factors to the measured PM2.5 concentration for the traffic site in Thessaloniki in percentage

6.3.6 Results for Stuttgart

Reliable results could not be obtained for the city of Stuttgart due to the high uncertainty of the measurements as the difference between the measured mass and the calculated PM2.5 mass as the sum of the species diverged substantially for most of the samples. This is probably due to weighing errors and have led to mathematical correctly solutions without physical sense.

7 Results comparison for the models used in ICARUS project

The results of the Lenschow approach and the PMF have been compared with the results obtained with the PCA and the PMF models applied by NCSRD for the same data sets as running more than one model on the same dataset can mutually validate their outputs and lead to more robust results.

7.1 Intercomparison for Athens

The following bar graph shows the PM2.5 source contribution obtained by the different models for Athens in the three sites (regional background, urban background and traffic site).

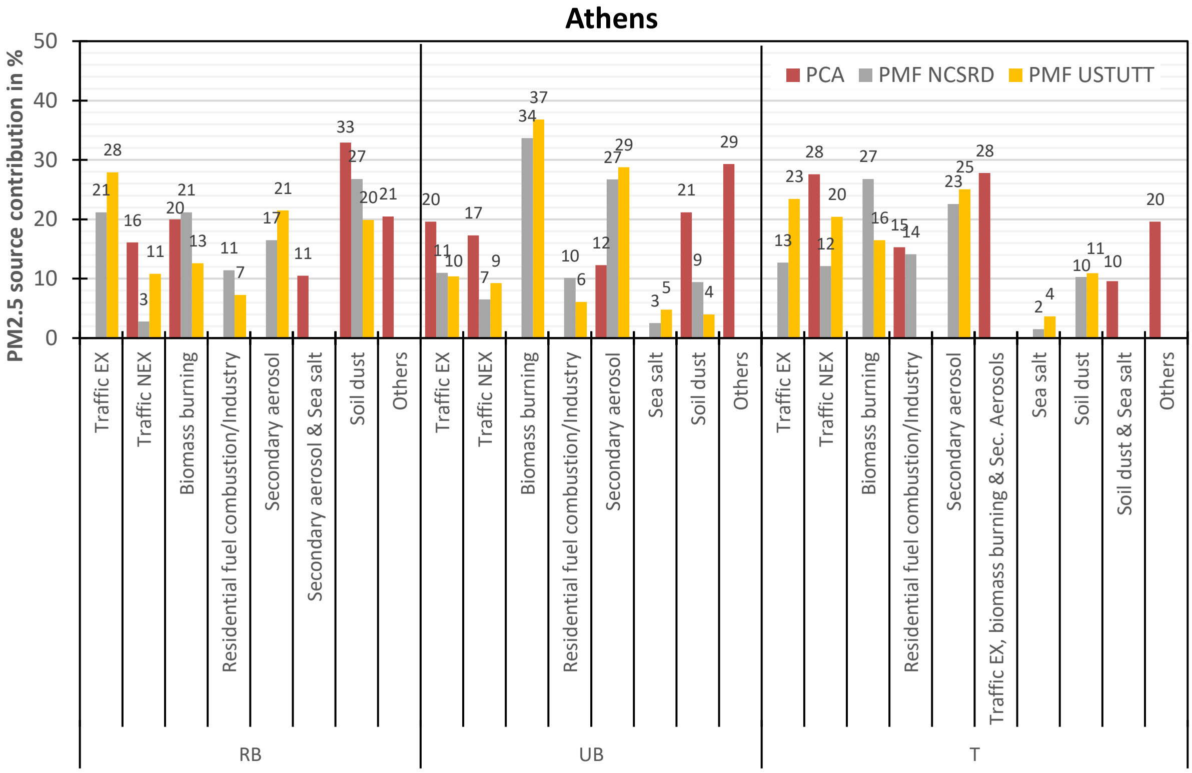


Figure 7.1. Comparison of PM2.5 source contributions among models tested at the three measurements sites in Athens.

As can be seen in Figure 7.1, similar results have been obtained among the models. Regarding the exceptions, the rural background shows for the traffic non-exhaust source a low percentage (3 %) modelled by PMF NCSRD. This can be explained due to the organic carbon content found associated with that source. For the PCA and the PMF USTUTT was higher which leads to higher PM2.5 concentrations as organic carbon is one of the major specie that contributes to the PM2.5 mass.

Another exception can be seen for the traffic related sources modelled by PMF NCSRD which present lower contribution than PMF USTUTT. The explanation is again due to the concentration of OC (which is cero for the source traffic NEX modelled by PMF NCSRD) and the high content of aerosols (SO_4^{2-} and NO_3^-) that have been associated with traffic EX modelled by PMF USTUTT that also have big impact in the final percentage of the sources.

It is worth mentioning that the PCA method could not identify 20 % of the sources (29 % for the urban background site) and that some of the factors were the sum of closely-related sources like traffic EX, biomass combustion and secondary aerosols.

In general, secondary aerosols, biomass burning (primarily in winter but with a small presence in summer due to the burning of agricultural wastes) and emissions from traffic are the main sources of PM2.5 in Athens. It is worth mentioning that the traffic exhaust source has its highest contribution in the regional background (25 % approx.) that can be associated to the transit of heavy-duty vehicles. The contribution of soil dust is also important, with occasional dust events along the year. Fuel oil combustion/industry has also been identified as a source of PM2.5 with higher contribution in winter than in summer. A small contribution of sea salt has also been detected.

7.2 Intercomparison for Brno

The following bar graph (Figure 7.2)shows the PM2.5 source contribution obtained by the different models for Brno in the three sites (regional background, urban background and traffic site).

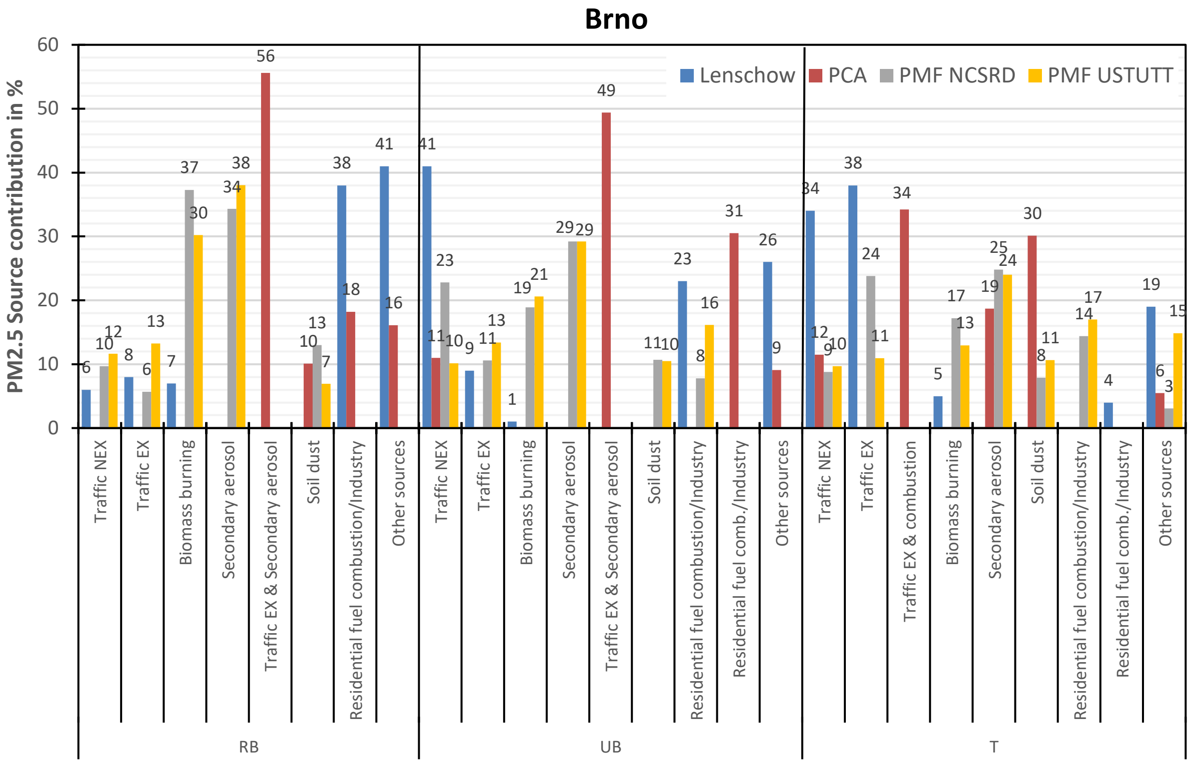


Figure 7.2. Comparison of PM2.5 source contributions among models applied for three measurements sites in Brno.

As shown in Figure 7.2, analogous percentages have been obtained between the PMF models and also the PCA model as the sum of different sources. The main differences between the models are explained below.

The Lenschow approach shows for the regional background a high peak for residential fuel combustion and industry that has not been identified by the PMF models. It is worth mentioning that the residential fuel combustion/industry category has been calculated for the Lenschow approach as the sum of households (this includes domestic biomass burning) and the industry, which explains why the peak is more similar to the biomass burning percentage modelled by the PMF models. The biomass burning for the Lenschow approach only accounts for the agriculture source.

Same explanation can be derived for the peak belonging to Lenschow approach Traffic NEX in the urban background and the traffic site, which counts also the resuspension of soil dust. It is however, higher than the sum of traffic NEX and soil dust of the other models in both stations.

The main difference observed in the urban background site is localised between the traffic EX modelled by PMF NCSRD and the other two receptor models due to the association of Cl element to the former one. As can be observed, species with similar temporal pattern are not always associated correctly by the PMF method.

The traffic site shows in the traffic EX source a low percentage modelled by PMF USTUTT, due to the content of organic and elemental carbon, which is lower than expected. Furthermore, the category "other source" presents high deviation between the PMF models. This category was identified as fireworks for both PMF models. The reason why the percentage of the source modelled by PMF USTUTT is higher than expected (15 % compared to 3 % from PMF NCSRD) is that, as was explained in Figure 6.16, the traffic NEX and the firework sources were not clearly identified by the model.

In general, biomass burning and secondary aerosols have the highest contribution to the PM2.5 mass in Brno, especially in the regional and urban background where they contribute together more than the 50 % of the PM2.5 concentration. Traffic related emissions contributes in higher share in the traffic and urban background sites than in the regional background. Soil dust and residential fuel combustion/industry category are also present in the three sites although their contribution is not higher than 20 %. Sporadic activities like fireworks have also been observed.

7.3 Intercomparison for Ljubljana

The following bar graph shows the PM2.5 source contribution obtained by the different models for Ljubljana in the three sites (regional background, urban background and traffic site).

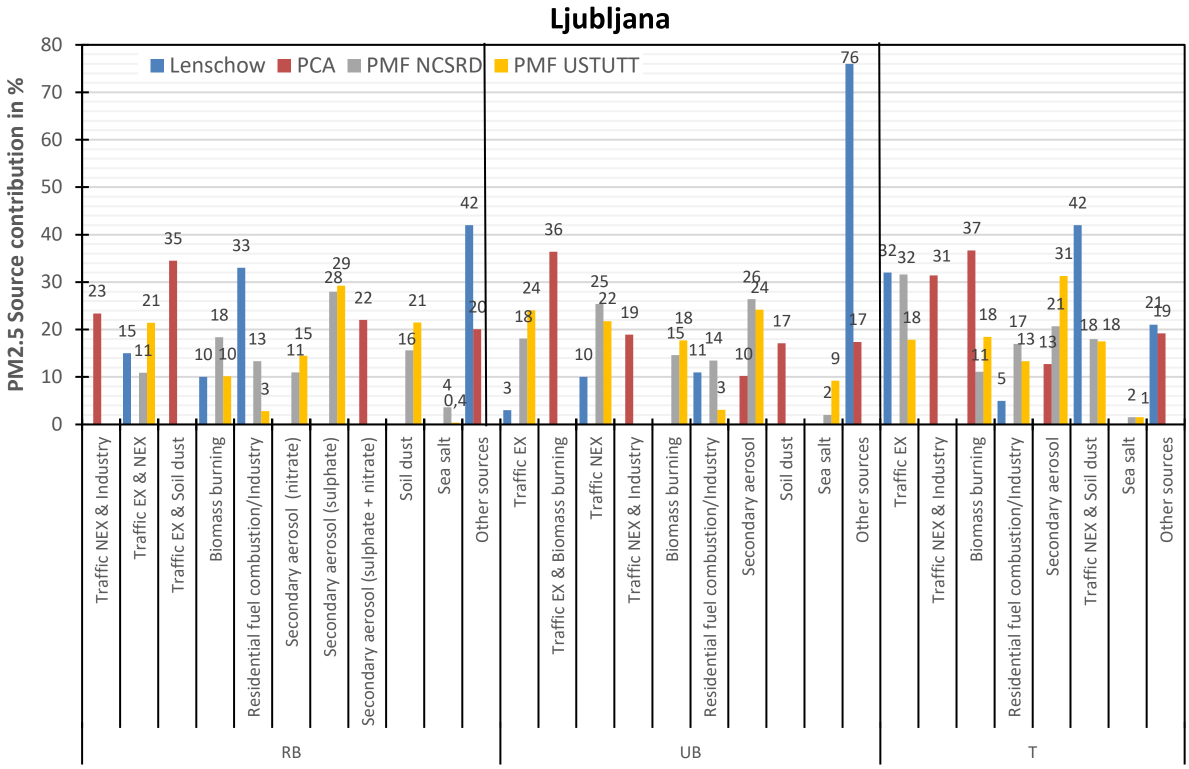


Figure 7.3. Comparison of PM2.5 source contributions among models tested at the three measurements sites in Ljubljana.

As can be seen in Figure 7.3, due to the high concentration of unknown material, the Lenschow approach results show in the urban and regional background sites high proportion of “other sources” category (42 and 76 %, respectively). A difference in the results can also be seen in the residential fuel combustion/industry between the PMF models in these two sites due to the organic carbon content associated.

The urban background station shows similar results among the receptor models except for the already mentioned residential fuel oil combustion/industry category and sea salt. The latter is due to the fact that the percentage of Cl associated to that source varies between the PMF models, that is 40 % for PMF NCSRD and 60 % for PMF USTUTT. In both cases, the Na^+ contribution was 70 %.

Regarding the traffic site, the only difference can be seen between the traffic exhaust gas source and the secondary aerosols for the PMF models. The former one can be explained due to the carbon content, reaching 40 % for PMF NCSRD and approximately 20 % for PMF USTUTT, which makes the traffic exhaust contribution modelled by PMF NCSRD to double the traffic exhaust contribution modelled by PMF USTUTT. The difference between the secondary aerosols contribution is made by the content of NO_3^-.

In general, up to 30 % of the contribution to PM2.5 are emissions coming from secondary aerosols, up to 20 % from biomass burning. Traffic related are also present from 11 % (in the regional background) and up to 32 % in the traffic site. Residential fuel combustion/industry contributes aprox. 15 %. Natural sources like soil dust and sea salt play a role in the PM2.5 mass, contributing on average 15 and 2 %, respectively.

7.4 Intercomparison for Madrid

The following bar graph shows the PM2.5 source contribution obtained by the different models for Madrid in the three sites (regional background, urban background and traffic site).

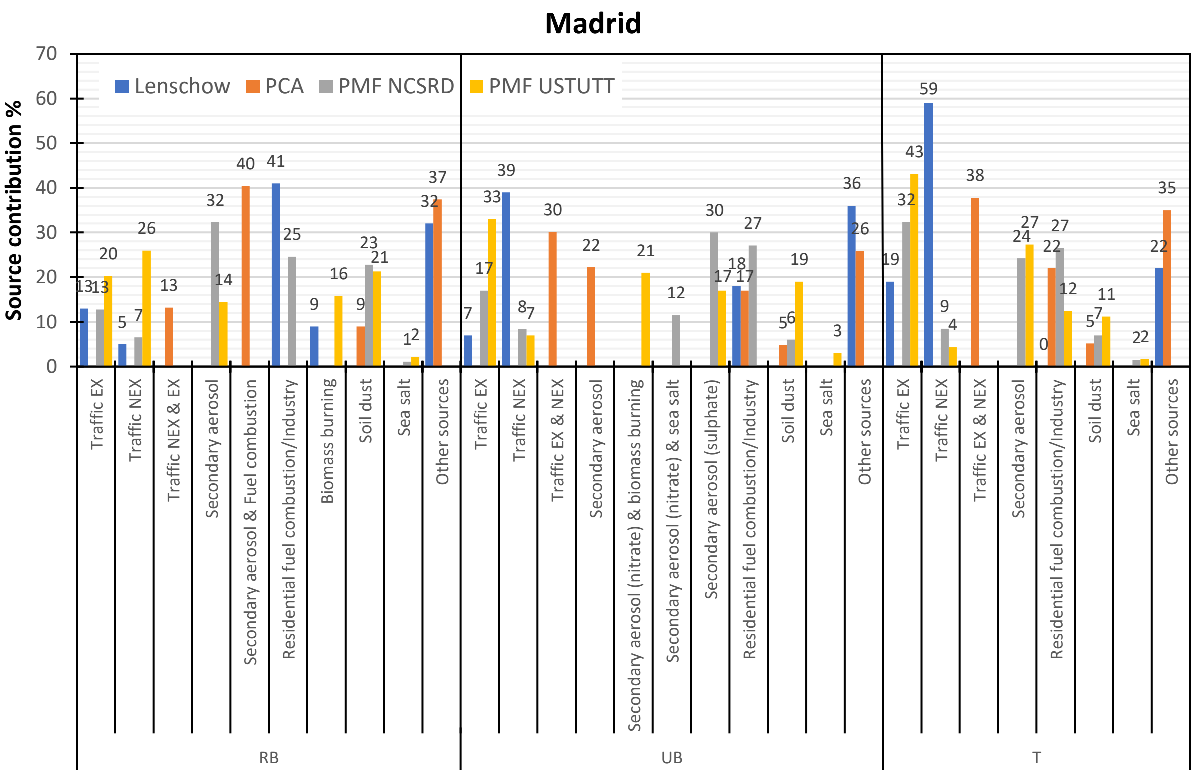


Figure 7.4. Comparison of PM2.5 source contributions among models tested at the three measurements sites in Madrid.

As shown in Figure 7.4, different sources have been identified among the models. The main differences are explained below.

In the rural background, a higher percentage is observed for the traffic non-exhaust sources contribution modelled by PMF USTUTT (26 %). This is explained by the high amount of Na^+ and Mg^{2+} associated to that source that could be due to the resuspension of aged salt. In the case of the secondary aerosols, part of the nitrates has been linked to biomass combustion as the present similar temporal pattern (higher in winter than in summer), resulting in lower percentages for the secondary aerosol source modelled by PMF USTUTT. The PCA soil dust contribution is relatively lower than the modelled by the PMF methods and the Lenschow approach has similar results as the receptor models.

In the urban background, the traffic exhaust sources show different results for the PMF USTUTT due to the SO_4^{2-} associated to it (23 %). PMF NCSRD model has found the nitrates associated with sea salt whereas PMF USTUTT with biomass burning. Soil dust was also modelled as having higher contribution by PMF USTUTT model due to the concentration of Ca^{2+}, as was not used for PMF NCSRD and for the PCA Ca^{2+}concentration appear also in the fuel oil combustion.

It is worth mentioning the high contribution of the traffic-related categories to the PM2.5 in the traffic site, which is 78, 38, 41 and 47 % for the Lenschow, the PCA the PMF NCSRD and the PMF USTUTT, respectively. As can be seen the Lenschow approach overestimates the contribution of this source.

In general, traffic is the prevailing source in both urban background and traffic sites and the highest compared to the rest of the participating cities. Moreover, Madrid is also the city where the residential combustion/industry source has the highest contribution in the three sites. However, it should be mentioned that no biomass burning source has been identified in the urban and background areas. Aerosols in the form of nitrates and sulphates contribute to the PM2.5 as the second prevailing source. Soil dust is present mainly in the regional site and it shows also the highest contribution to PM2.5 compared to the other cities, closely followed by the regional background sites in Ljubljana and Athens. A small contribution of sea salt has also been detected.

7.5 Intercomparison for Thessaloniki

The following bar graph (Figure 7.4) shows the PM2.5 source contribution obtained by the different models for Thessaloniki in the three sites (regional background, urban background and traffic site).

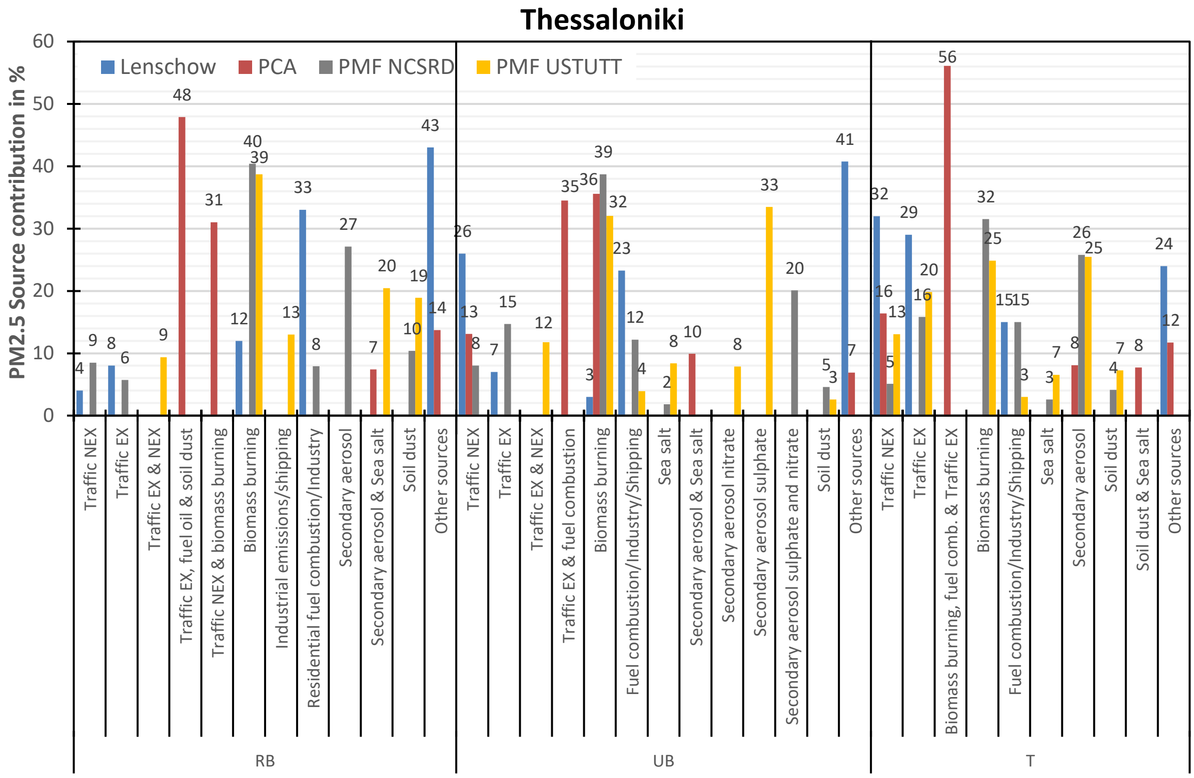


Figure 7.5. Comparison of PM2.5 source contributions among models tested at the three measurements sites in Thessaloniki.

As can be seen in Figure 7.5, different combination of sources has been found for the regional background site in Thessaloniki. The Lenschow approach shows similar results with respect to traffic related sources and comparing the residential fuel combustion/industry with the biomass combustion source (33 and 39 %, respectively). Difference in the soil dust associated to the PMF models can be explained due to the concentration of organic and elemental carbon associated to the source modelled by PMF USTUTT (12 and 10 %, respectively).

Urban background shows differences due to the association of the inorganic aerosols in different contributions. For PMF USTUTT both sulphates and nitrates were identified as different factors with high contribution to the factor 63 and 60 % respectively whereas for PMF NCSRD the species concentration in the unique factor identified were approximately 40 % for both sulphates and nitrates aerosols. The rest of the mass where found associated to traffic EX for the nitrates and to fuel combustion/ industry/ shipping for sulphates.

Regarding the traffic site, differences in the traffic non-exhaust sources appear between the PMF models as the species have been mixed with the fuel combustion/industry and shipping category. The Lenschow approach has overestimated the contribution of the traffic sources, as happened in Brno. The PCA shows similar results except for the secondary aerosols.

In general, Thessaloniki has the highest contribution of biomass burning to the PM2.5 mass in the regional background (40 %) and one of the highest in the urban background (35 %), together with the regional background in Brno and the urban background in Athens. On average, one quarter of the PM2.5 are coming from secondary inorganic aerosols (sulphates and nitrates). The relative traffic contribution to PM2.5 varies from the regional background (12 %) to the urban background (23 %) and the traffic site (27 %). Industry and emissions from the port as well as sea salt has also been observed, contributing up to 15 and 7 %, respectively.

7.6 Summary of the results

In Figure 7.7, the results of the six main PM2.5 sources found with the PMF models for the three measurement sites (regional background, urban background and traffic site) for the 5 evaluated cities (Athens, Brno, Ljubljana, Madrid and Thessaloniki) are shown.

The information contained in the boxplots is shown in Figure 7.6.

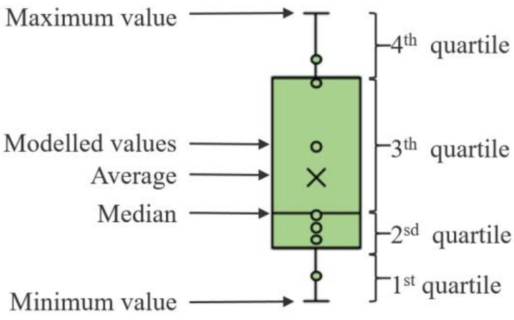


Figure 7.6. Information contained in the boxplots.

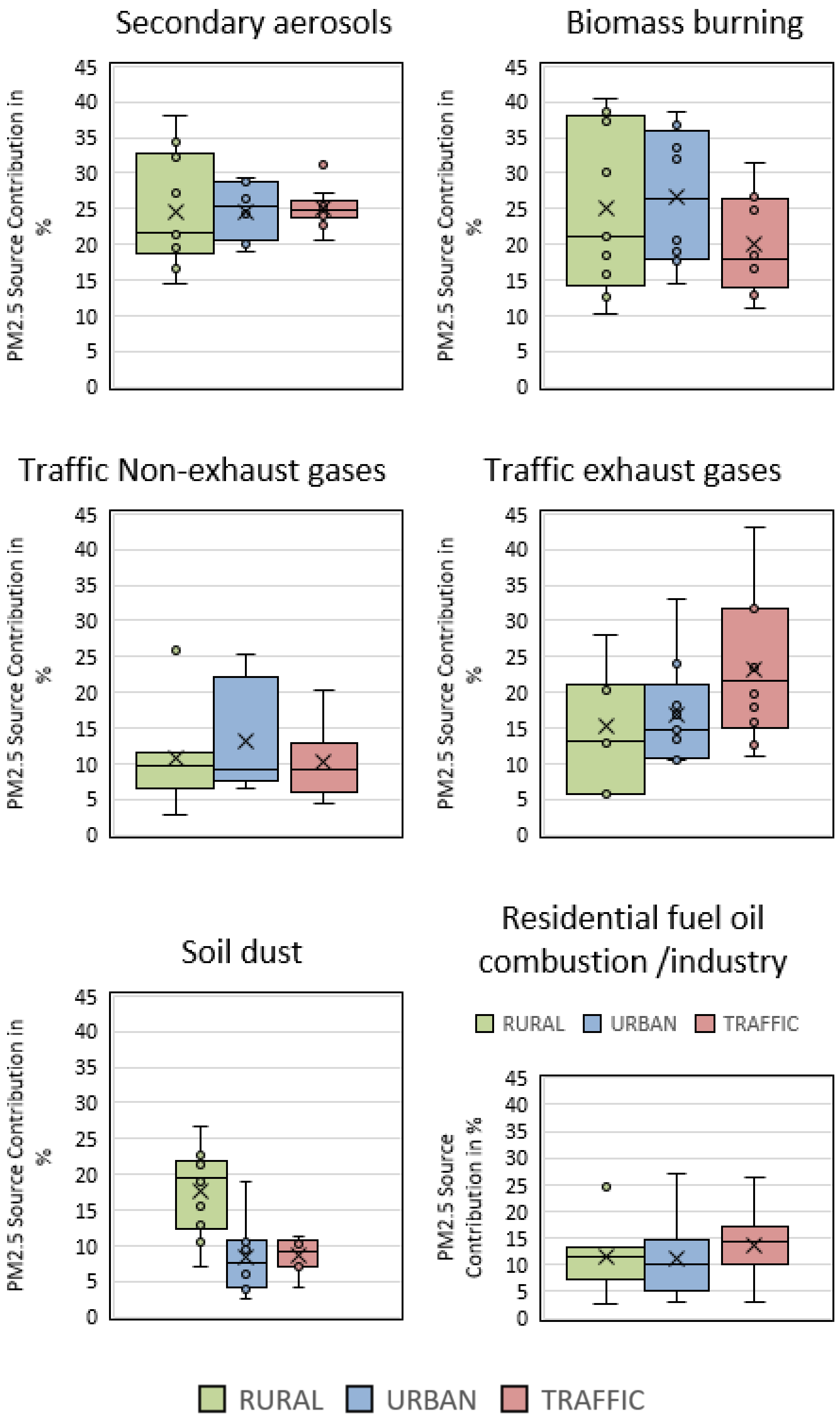


Figure 7.7. Boxplots for the source apportionment of PM2.5 modelled by PMF models

As can be seen from Figure 7.7, an average contribution to PM2.5 of 24 ± 7 % have been found for the secondary aerosols. The highest contribution was observed in the regional background in Brno (38 %) and the lowest in the regional background in Madrid (14 %). This source is relatively stable when comparing all the stations and it includes in some cases secondary organic carbon. From the emission inventories used for the Lenschow approach it was deduced that the main sources of inorganic aerosols in cities are industry, agriculture, traffic and residential heating, as they emit the precursors (SO_2, NO_2, NH_3, and NMVOCs). Furthermore, maritime aerosols have been observed in the cities closed to the Mediterranean Sea. The average contribution to the PM2.5 is 3 ± 2 % and the maximum contribution was found in the urban background station in Ljubljana (9 %).

Biomass burning is also a prevailing source of PM2.5 during the cold season (24 ± 10 %), ranging from 11 % in the traffic site in Ljubljana to 40 ± 1 % in the regional background site in Thessaloniki. Therefore, controls on biomass burning are important measures to reduce particle matter, especially during winter. In the cities like Madrid where a biomass burning factor could not be identified or the factor was a combination of sources, as it is the case in the traffic and urban background sites, respectively, an increase in the fuel oil combustion/industry category was observed (27 %) compared to the average contribution in the rest of the participating cities (12 ± 7 %). It is worth mentioning the contribution of the shipping activities to fuel oil combustion/industry category in Thessaloniki and that significantly amounts of Pb have been measured in the three sites in Thessaloniki and in the regional background in Athens.

The highest contribution of the traffic exhaust sources to the PM2.5 was found in the urban site in Madrid (43 %) and the lowest in the regional backgrounds in Thessaloniki and Brno (6 %). The highest contribution of emissions coming from the brake and tyre wear, together with resuspended mineral dust particles and road wear material, was observed in the rural background site in Madrid (26 %) and the lowest in the regional background in Athens (3 %). That implies that there is not a clear correlation between the non-exhaust sources and the type of site. However, the tendency is clear for exhaust sources, observing the lowest average in regional background (15 ± 7 %) and the highest average in traffic sites (21 ± 12 %).

Soil dust contributes also to the PM2.5 mass with an average of 12 ± 7 %. The highest contribution of this natural source was found in the regional background in Athens (27 %), whereas the lowest was observed in urban background in Thessaloniki (3 %). Some of the tracers of soil dust (Ca, Fe, Ti) where in several occasions identified as resuspension due to road traffic and hence associated with traffic non-exhaust sources.

8 Reproducibility

As was discussed in Chapter 7, the intercomparison exercise led to the validation of the receptor models and the rejection of the Lenschow approach as an adequate method to define air policy measures. As it was reported by Thunis (2018), the incremental approach, which is the first step for the Lenschow approach, leads to an underestimation of the local contribution ranging from 30 to 50 % for medium and large size cities and it is maintained that the selection of the stations is a critical step.

In regard to the representativeness of the monitoring stations, in some of the participating cities the regional station was located less than 10 km form the city centre, namely in Madrid and in Ljubljana, which corresponds more to a near-city background station. In a near-city background station the distance to large pollution source is from 3 to 10 km (more information concerning the measurement station areas of the six participating cities can be found in the Annex). Other cities presented industrial activities that were less than 5 km to the regional background site, namely Athens, Ljubljana and Thessaloniki. Thus, the proposed assumption that the urban impact at the regional background site is negligible is not fulfilled for the Lenschow approach.

In order to enable comparison of air quality across Europe, the EuroAirnet (European Air Quality monitoring network) in cooperation with the European Environment Agency proposed a classification criteria for monitoring stations. According to their criteria, a regional/rural background station should have a minimum distance to the emission sources of 10 – 50 km (EuroAirnet, 1999).

Concerning the receptor models, in general terms a good correlation between them have been observed. It should be mentioned that the Principal Component Analysis identified in most of the cases a combination of the sources which makes difficult the comparison with other receptor models.

The differences between the PMF models could have several origins. The most probable ones are listed below:

- The input data (concentration and uncertainties). Although the datasets were there same, the user of the EPA PMF 5.0 software can choose whether to exclude a sample or not in the preliminary data check according to the temporal variation of the species. In this particular case, the concentration of PM2.5 was also included in the PMF models run by USTUTT and downweighed to “weak species”.

- The classification of the species in the three possible categories (strong, bad, weak). It depends to the signal-to-noise (S/N) ratio which is highly influenced by the uncertainties. After analysing the residuals and the data fit of the model the user can downweigh the species that do not present a good correlation between the predicted data and the observed data.

- The extra model uncertainty. Whereas the extra model uncertainty of the PMF model run by NCSRD was adjusted from 8 to 12 %, the extra model uncertainty of the PMF model run by USTUTT was in all cases 10 %.

- The expertise of the user. A weakness of PMF is that individual sources are not always distinguished, as the user has to discriminate between factors explaining emission sources, in which tracers sharing emission sources are grouped, and factors explaining formation/transformation processes (e.g. secondary nitrates and sulphates). In these situations, the experience of the scientist plays a significant role.

- Constrains. This tool allows the user to constrain or “pull” elements in the solution, if source profiles or contributions are known for some factors or samples. The constrains reported from both institutions were not the same for all the measurement sites. These elements should always be justified.

Furthermore, Positive Matrix Factorization software includes three error estimation methods for analysing factor solutions: bootstrap (BS), displacement of factor elements (DISP), and bootstrap enhanced by displacement (BS-DISP). These methods capture the uncertainty of PMF analyses due to random errors and rotational ambiguity, as was explained in subchapter 6.2. Hence, these tools allow different users to reach the same mathematically and physically correct solution.

9 Summary and conclusions

The scope of this thesis is to present the results of source apportionment by applying the Lenschow approach and the PMF method on PM2.5 data collected in six European cities (Athens, Brno, Ljubljana, Madrid, Thessaloniki and Stuttgart) in the frame of the ICARUS project. The PM2.5 chemical composition was evaluated for two different campaigns: one during the summer and the other during the winter season and in three different stations of each city: regional background, urban background and traffic.

The evaluation of the chemical composition of the PM2.5 samples allowed us to find the major chemical groups contributing to the concentration of PM2.5. These are organic matter coming from the organic carbon analysis, elemental carbon, aerosols (SO_4^{2-}, NO_3^-, NH_4^+), cations (K^+, Na^+), ions (Cl^-) and metals (Ca, Fe). The participation of these species to the final PM2.5 concentration measured depends on the location of the measurement station and the weather conditions, among other parameters. However, it can be concluded that organic matter and sulphate are the dominant species in the $PM_{2.5}$ mass. Nitrate belongs to this category only in winter due to its temperature-dependent formation.

After the evaluation and comparison of the results obtained by the Lenschow approach with other models (PCA and PMF), it can be concluded that the Lenschow approach can only be used as a qualitative method and cannot be used to design strategies for urban air quality planning as the preliminary assumptions are not fulfilled in many cities. Moreover, it has been derived that the measurement site selection is crucial for the well performance of the model, that is, each species measured in the traffic site must have higher concentration than in the urban background station on the same day and the same condition must apply between the urban and the regional background. However, as we have seen from the results, this is not always the case, as proven by the city of Athens or the winter campaign in Madrid.

The emission inventories used for the Lenschow approach do not specify information regarding natural sources hence, their estimation is a source of uncertainty. The presence of unknown sources due to the unidentified material also contributes to increase the uncertainty of the approach. Furthermore, the discarded species due to negative subtraction between the values of the measurement sites reduce the number of available samples, which are in some cases not enough data to be representative.

Practically wise, using a method that mathematically interconnects the results of three stations has several risks as the measurements are totally compromised to be done simultaneously. Because of this condition, several samples that were already analysed were discarded for the Lenschow approach, so that valuable information could not be used.

Based on the application of the Positive Matrix Factorization model, 5 to 7 factors have been identified to be the sources of PM2.5. As have been seen from the results, although an average of the source contribution to PM2.5 can be inferred, high variations are observed from one city to another and from different types of measurement sites. Hence, geographical and seasonal variation should be taken into account for the effective and efficient planning of air quality actions.

10 Literature

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11 Annex

Information regarding the sampling sites and the sampling campaign.

Table 11.1. Information regarding the measurement sites and the sampling campaigns.

City	**Athens** (NCSRD)			**Brno** (MU)			**Ljubljana** (JSI)		
Station	**T**	**U**	**R**	**T**	**U**	**R**	**T**	**U**	**R**
Abbreviation	AR	AGP	AL	KT	LA	KS	MOL	ARSO	TETOL
Period for the Winter Campaign	24/01/2017 - 09/03/2017			03/02/2017 - 07/03/2017			20/02/2017 - 25/03/2017		
Winter campaign (samples + blanks)	39 + 3	37 + 3	37 + 3	30 + 2	30 + 2	30 + 1	30 + 1	30 + 1	29 + 1
Period for the Summer Campaign	23/05/2017 - 20/07/2017			12/06/2017 - 13/07/2017			15/05/2017 - 13/06/2017		
Summer campaign (samples + blanks)	36 + 3	31 + 3	35 + 3	30 + 3	30 + 3	30 + 2	28 + 2	30 + 2	29 + 2
Traffic intensity at the infront road	high	medium	low	high	medium	low	high	medium	low
Distance from the high traffic avenue/highway	3m	400 m	500 m	3m	520 m	1000 m	150 m	230 m	650 m
Distance from the city center			101 km			130 km			7 km
frequent transist of heavy road vehicles	no	no	yes	no	yes	no	no	no	yes
Industrial activity	10 km	>20 km	0,5 km	3 km	1,7 km	no	1 km	0,5 km	2 km
Vegetation	no	yes	yes	yes	yes	yes	yes	no	no
Agricultural activities	no	no	yes	no	yes	yes	no	no	yes
Domestic heating	liquid fuel, gas, electric devices, fireplaces	liquid fuel, gas, electric devices, fireplaces	gas, electric devices, fireplaces	gas, electric devices	liquid fuel, gas, electric devices, fireplaces	gas, electric devices, fireplaces, coal	liquid fuel, gas, electric devices, wood	liquid fuel, gas, electric devices, wood	liquid fuel, gas, electric devces, wood

Table 11.1 (continuation)

City	**Madrid** (ISCIII)			**Thessaloniki** (AUTH)			**Stuttgart** (USTUTT)		
Station	**T**	**U**	**R**	**T**	**U**	**R**	**T**	**U**	**R**
Abbreviation	ES	FA	CA	UNV	STV	NE	HS	BC	SA
Period for the Winter Campaign	19/02/2017 - 5/03/2017			08/02/2017 - 15/03/2017			26/01/2018 - 17/03/2018		
Winter campaign (samples + blanks)	31 + 2	31 + 2	31 + 2	36 + 3	36 + 3	34 + 3	26 + 2	26 + 2	26 + 2
Period for the Summer Campaign	22/06/2017 - 11/08/2017			26/06/2017 - 08/08/2017			26/08/1017 - 10/10/2017		
Summer campaign (samples + blanks)	29 + 1	24 + 3	31 + 3	31 + 3	31 + 3	33 + 3	27	27	27
Traffic intensity at the in-front road	high	low	low	high	medium	low	high	medium	low
Distance from the high traffic avenue/highway	25 m	1000 m	2500 m	37 m	675 m	5000 m	2 m	30 m	2900 m
Distance from the city center			3, 5 km			15 km			50 km
frequent transist of heavy road vehicles	no	no	no	yes	no	no	no	no	no
Industrial activity	no	no	no	10 km	6 km	5 km	no	1 km	no
Vegetation	yes	yes	yes	yes	no	yes	yes	yes	yes
Agricultural activities	no	no	no	no	no	yes	no	no	yes
Domestic heating	liquid fuel, gas, electric devices	liquid fuel, gas	liquid fuel, gas, electric devices	liquid fuel, gas	liquid fuel, gas, fireplaces	liquid fuel, fireplaces	liquid fuel, gas, electric devices, wood	liquid fuel, gas, electric devices, wood	liquid fuel, gas, electric devices, wood

Conversion chart for aggregated sector groups

Table 11.2. Conversion chart for aggregated sector groups used in Lenschow approach

NFR09 Code	NFR09 Longname	Aggregated sector name
1 A 1 a	Public electricity and heat production	Industry
1 A 1 b	Petroleum refining	Industry
1 A 1 c	Manufacture of solid fuels and other energy industries	Industry
1 A 2 a	Stationary combustion in manufacturing industries and construction: Iron and steel	Industry
1 A 2 b	Stationary Combustion in manufacturing industries and construction: Non-ferrous metals	Industry
1 A 2 c	Stationary combustion in manufacturing industries and construction: Chemicals	Industry
1 A 2 d	Stationary combustion in manufacturing industries and construction: Pulp, Paper and Print	Industry
1 A 2 e	Stationary combustion in manufacturing industries and construction: Food processing, beverages and tobacco	Industry
1 A 2 f i	Stationary combustion in manufacturing industries and construction: Other (Please specify in your IIR)	Industry
1 A 2 f ii	Mobile Combustion in manufacturing industries and construction	Industry
1 A 3 a ii (i)	Civil aviation (Domestic, LTO)	Non-road transport
1 A 3 a i (i)	International aviation (LTO)	Non-road transport
1 A 3 b i	Road transport: Passenger cars	Exhaust sources
1 A 3 b ii	Road transport: Light duty vehicles	Exhaust sources
1 A 3 b iii	Road transport: Heavy duty vehicles	Exhaust sources
1 A 3 b iv	Road transport: Mopeds & motorcycles	Exhaust sources
1 A 3 b v	Road transport: Gasoline evaporation	Exhaust sources
1 A 3 b vi	Road transport: Automobile tyre and brake wear	Tyre abrasion and resuspension
1 A 3 b vii	Road transport: Automobile road abrasion	Tyre abrasion and resuspension
1 A 3 c	Railways	Non-road transport
1 A 3 d ii	National navigation (Shipping)	Non-road transport
1 A 4 a i	Commercial / institutional: Stationary	Households
1 A 4 a ii	Commercial / institutional: Mobile	Households
1 A 4 b i	Residential: Stationary plants	Households
1 A 4 b ii	Residential: Household and gardening (mobile)	Households
1 A 4 c i	Agriculture/Forestry/Fishing: Stationary	Households
1 A 4 c ii	Agriculture/Forestry/Fishing: Off-road vehicles and other machinery	Non-road transport
1 A 5 a	Other stationary (including military)	Households
1 A 5 b	Other, Mobile (including military, land based and recreational boats)	Households
1 B 1 a	Fugitive emission from solid fuels: Coal mining and handling	Industry
1 B 1 b	Fugitive emission from solid fuels: Solid fuel transformation	Industry
1 B 2 a i	Exploration, production, transport	Industry

1 B 2 a iv	Refining / storage	Industry
1 B 2 a v	Distribution of oil products	Industry
1 B 2 b	Natural gas	Industry
1 B 2 c	Venting and flaring	Industry
2 A 1	Cement production	Industry
2 A 2	Lime production	Industry
2 A 7 a	Quarrying and mining of minerals other than coal	Industry
2 A 7 b	Construction and demolition	Industry
2 A 7 c	Storage, handling and transport of mineral products	Industry
2 B 1	Ammonia production	Industry
2 B 2	Nitric acid production	Industry
2 B 3	Adipic acid production	Industry
2 B 4	Carbide production	Industry
2 B 5 a	Other chemical industry	Industry
2 B 5 b	Storage, handling and transport of chemical products	Industry
2 C 1	Iron and steel production	Industry
2 C 2	Ferroalloys production	Industry
2 C 3	Aluminium production	Industry
2 C 5 a	Copper production	Industry
2 C 5 b	Lead production	Industry
2 C 5 c	Nickel production	Industry
2 C 5 d	Zinc production	Industry
2 C 5 e	Other metal production	Industry
2 D 1	Pulp and paper	Industry
2 D 2	Food and drink	Industry
2 D 3	Wood processing	Industry
3 A 1	Decorative coating application	Industry
3 A 2	Industrial coating application	Industry
3 B 1	Degreasing	Industry
3 B 2	Dry cleaning	Industry
3 C	Chemical products	Industry
3 D 1	Printing	Industry
3 D 2	Domestic solvent use including fungicides	Industry
3 D 3	Other product use	Industry
4 A 1	Cattle	Agriculture
4 B 1 a	Cattle dairy	Agriculture
4 B 1 b	Cattle non-dairy	Agriculture
4 B 2	Buffalo	Agriculture
4 B 3	Sheep	Agriculture
4 B 4	Goats	Agriculture
4 B 5	Camels an Lamas	Agriculture

4 B 6	Horses	Agriculture
4 B 8	Swine	Agriculture
4 B 9 a	Laying hens	Agriculture
4 B 9 b	Broilers	Agriculture
4 B 9 c	Turkeys	Agriculture
4 B 9 d	Other poultry	Agriculture
4 B 12	Liquid System	Agriculture
4 B 13	Other (Solid storage and dry lot)	Agriculture
4 C 4	Other	Agriculture
4 D 1	Direct soil emissions	Agriculture
4 D 1 a	Synthetic N-fertilizers	Agriculture
4 D 2 a	Farm-level agricultural operations including storage, handling and transport of agricultural products	Agriculture
4 e	Prescribed Burning of Savannahs	Agriculture
4 F	Field burning of agricultural wastes	Agriculture
6A	Solid waste disposal on land	Waste treatment and disposal
6 B	Waste-water handling	Waste treatment and disposal
6 B 1	Industrial Wastewater	Waste treatment and disposal
6 B 2	Domestic and Commercial Wastewater	Waste treatment and disposal
6 C a	Clinical waste incineration (d)	Waste treatment and disposal
6 C b	Industrial waste incineration (d)	Waste treatment and disposal
6 C c	Municipal waste incineration (d)	Waste treatment and disposal
6 C e	Small scale waste burning	Waste treatment and disposal
6 D	Other waste (e)	Waste treatment and disposal
7A	Other (included in national total for entire territory)	Waste treatment and disposal