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# SOURCE APPORTIONMENT STUDY FOR KUMANOVO URBAN AREA

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AMBICON.UGD

This study was prepared by the AMBICON laboratory at Goce Delcev University—Stip as part of the "Scaling-up Actions to Tackle Air Pollution" project, which is implemented by the United Nations Development Programme (UNDP) in partnership with the Ministry of Environment and Physical Planning, along with the municipalities of Kavadarci, Kumanovo, Gostivar, Struga, and Strumica.

The project is a component of the UNDP Framework Programme funded by Sweden. The Programme also includes the project “Building municipal capacities for project implementation”.

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## Symbols and abbreviations

For the purposes of this document, the following symbols and abbreviated terms apply.

| | |
|---|---|
| C | Concentration of PM (µg/m3) at ambient conditions |
| GUM | Guide to the Expression of Uncertainty in Measurement |
| JCGM | Joint Committee for Guides in Metrology |
| PM | Particulate Matter |
| PTFE | Polytetrafluoroethylene |
| QA/QC | Quality Assurance / Quality Control |
| NIST | National Institute of Standards and Technology |
| QCS | Quality Control Sample |
| AQIP | Academic Quality Improvement program |
| EEA | European Environment Agency |
| TSP | Total suspended particles |
| NMVOC | Non-methane volatile organic compounds |
| MOEPP | Ministry of environment and physical planning |
| ED-XRF | Energy dispersive X-ray fluorescence |
| IC | Ion chromatography |
| OC | Organic carbon |
| EC | Elemental carbon |
| SA | Source apportionment |
| SD | Standard deviation |
| C.V. | Coefficient of variation |

## Terms and definitions

For the purposes of this document, the following terms and definitions apply.

**Ambient air –** is outdoor air in the troposphere, excluding workplaces as defined by Directive 89/654/EEC [12] where provisions concerning health and safety at work apply and to which members of the public do not have regular access.

**Calibration** - operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication.

**Calibration Standard (CAL) -** a solution prepared from the stock standard solution(s) which is used to calibrate the instrument response with respect to analyte concentration.

**Certified reference material (CRM)** is defined as a “reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a reference material certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability”.

**Combined standard uncertainty** - standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities.

**Coverage factor** - numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty.

**Expanded uncertainty** - quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand.

**Field blank** - filter that undergoes the same procedures of conditioning and weighing as a sample filter, including transport to and from, and storage in the field, but is not used for sampling air, and it has the same treatment as samples.

**Instrument Detection Limit (IDL)** - the concentration equivalent of the analyte signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

**Internal Standard** - pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same solution. The internal standard must be an analyte that is not a sample component.

**Laboratory Reagent Blank (LRB) (Preparation Blank)** - an aliquot of reagent water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

**Linear Dynamic Range (LDR)** - the concentration range over which the analytical working curve remains linear.

**Limit value** - level fixed based on scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment, to be attained within a given period and not to be exceeded once attained.

**Method Detection Limit (MDL)** - the minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are intended as a guide to instrumental limits typical of a system optimized for multi-element determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual MDLs and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

**Performance characteristic** - one of the parameters assigned to a sampler to define its performance.

**Performance criterion** - limiting quantitative numerical value assigned to a performance characteristic, to which conformance is tested.

**Period of unattended operation** - time over which the sampler can be operated without requiring operator intervention.

**PMx** - particulate matter suspended in air which is small enough to pass through a size-selective inlet with a 50 % efficiency cut-off at x μm aerodynamic diameter.

**Quality Control Sample (QCS) -** a solution containing known concentrations of method analytes which is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

**Reference method (RM)** - measurement method(ology) which, by convention, gives the accepted reference value of the measurand.

**Sampled air -** ambient air that has been sampled through the sampling inlet and sampling system.

**Sampling inlet** - entrance to the sampling system where ambient air is collected from the atmosphere.

**Standard uncertainty -** uncertainty of the result of a measurement expressed as a standard deviation.

**Stock Standards Solutions** - a concentrated solution containing one or more analytes prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

**Suspended particulate matter** - notion of all particles surrounded by air in a given, undisturbed volume of air.

**Tuning Solution** - a solution used to determine acceptable instrument performance prior to calibration and sample analyses.

**Time coverage** - percentage of the reference period of the relevant limit value for which valid data for aggregation have been collected.

**Uncertainty (of measurement)** - parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand

**Weighing room blank** - filter that undergoes the same procedures of conditioning and weighing as a sample filter, but is stored in the weighing room

## 1. Introduction

The "Scaling-up actions to tackle air pollution" project is a component of the UNDP Framework Programme, funded by Sweden. The project is being executed in North Macedonia by the United Nations Development Program (UNDP), in partnership with the Ministry of Environment and Physical Planning, as well as the municipalities of Gostivar, Kavadarci, Kumanovo, Struga, and Strumica.

Building on the results and lessons learned from the first phase conducted in Skopje, the project aims to scale up and replicate the developed concept in five additional cities facing air pollution challenges: Gostivar, Kavadarci, Kumanovo, Struga, and Strumica. Following the successful completion of the Source Apportionment Study for the City of Skopje, the AMBICON Laboratory has been tasked with preparing the Source Apportionment Studies for the five new municipalities: Gostivar, Kavadarci, Kumanovo, Struga, and Strumica.

The primary objective of a source apportionment study is to collect insights regarding pollution sources and their contributions to ambient air pollution levels. This information is essential for developing effective air quality policies, which are necessary for the implementation of the Air Quality Directives (Directive 2008/50/EC and Directive 2004/107/EC).

The actions undertaken followed the rigorous study approach outlined in the European guide on air pollution source apportionment with receptor models (Revised edition 2019, JRC) and included:

- Preliminary evaluation of areas under examination (emission inventories, time series of pollutants and meteorology etc),
- Selection of representative receptors/monitoring sites,
- Sampling and chemical speciation,
- Construction of multivariate receptor model.

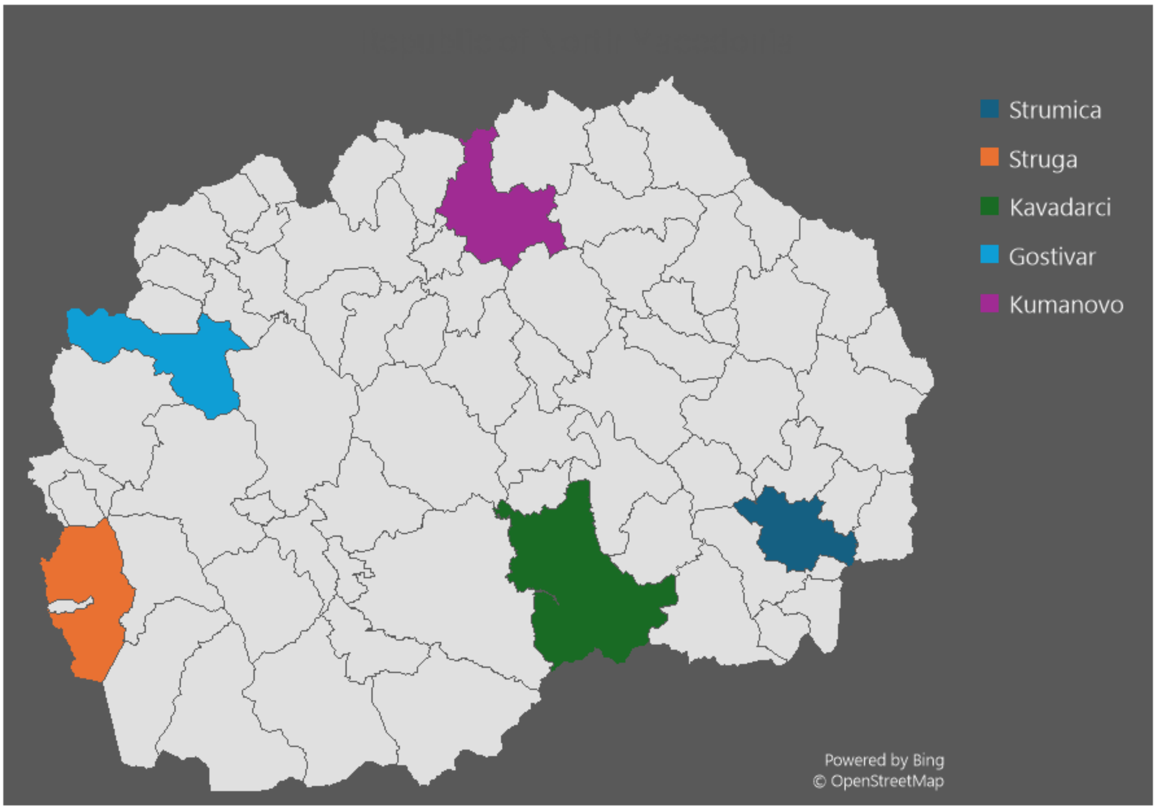


**Figure 1. Map of municipalities included in this study**

The project also included an indoor air quality study for ten selected public buildings—kindergartens and schools—across the urban areas of five pilot municipalities. The study aimed to assess the current air quality and develop strategies for creating a healthier indoor environment in these facilities.

This research represents one of the first efforts to provide quantitative information on the contributions of various pollution sources to ambient PM2.5 levels in urban centers outside the capital city's urban area. Consequently, the research produced a unique data set that could be used to improve air quality by addressing strategies for mitigating air pollution and implementing effective air protection measures.

## 2. Background information's

### 2.1. Kumanovo urban area

The Municipality of Kumanovo is located in the northeastern part of North Macedonia and is part of the Northeastern Statistical Region. The urban area of Kumanovo extends across the Kumanovo Valley (Žegligovo) at an elevation of 340 m, stretching on both sides of the Lipkovka and Kumanovka rivers. This means that the city of Kumanovo is situated at the intersection of the two most significant corridors in the country: Corridor 8 (East - West) and Corridor 10 (North - South).

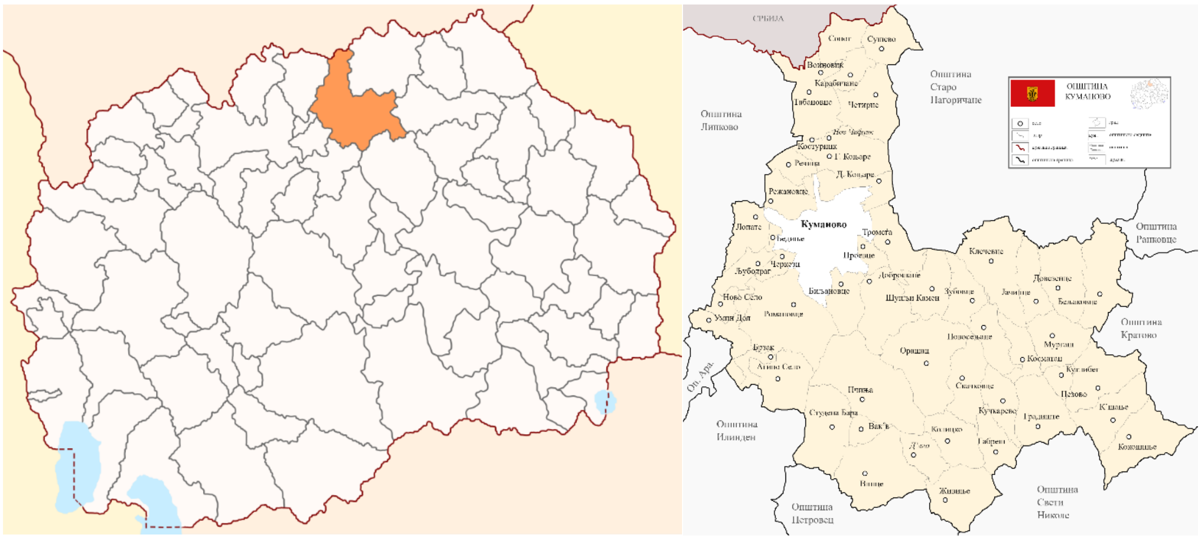


**Figure 2. Location of Municipalities of Kumanovo**

Kumanovo borders Serbia to the north and Staro Nagoricane to the northeast. It borders Kratovo to the east, Sveti Nikole to the southeast, and Petrovec and Ilinden to the southwest. Additionally, it borders the municipality of Lipkovo to the northwest and the municipality of Arachinovo to the west. The Municipality of Kumanovo covers an area of 1212 km$^2$, with 509.48 km$^2$ belonging to the city of Kumanovo [1].

According to the 2021 Census, Kumanovo had a total population of 98,104, which includes 30,450 households and 38,147 residential units, comprising both apartments and houses [2].

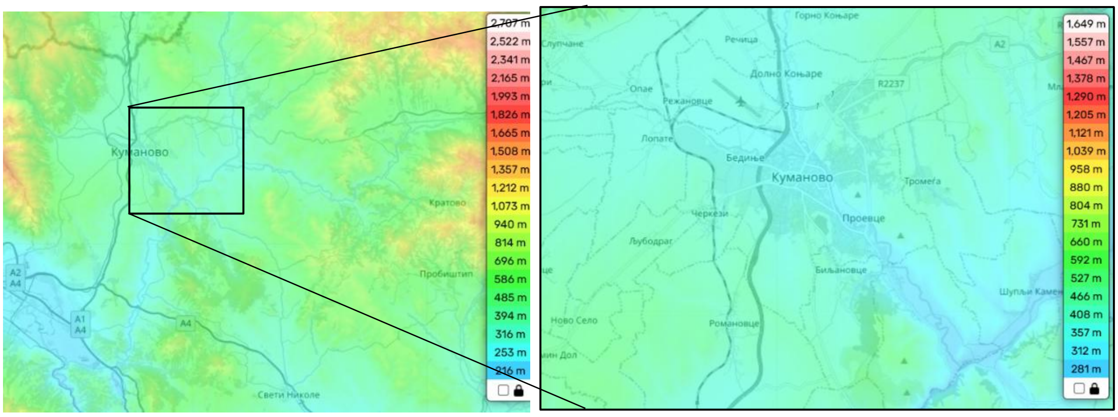


Figure 3. Kumanovo topography map [3]

## 2.2. Climate

The climate in the municipality of Kumanovo is characterized as temperate continental, featuring cold and wet winters as well as warm and dry summers throughout the year. The average annual temperature is approximately 11.8 °C, though it is lower on the slopes of the surrounding mountains, depending on altitude. The maximum average annual temperature can reach 17.6°C, while the minimum average annual temperature is 6.2 °C.

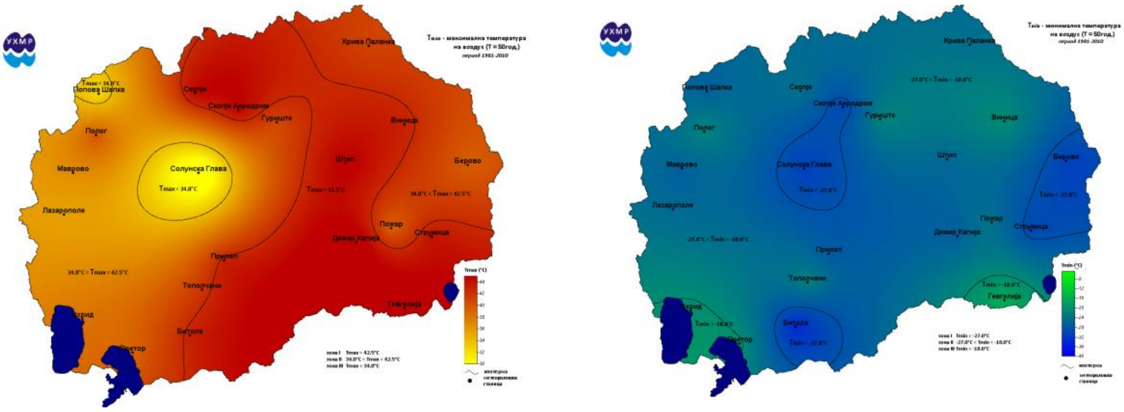


Figure 4. Maximum and minimum temperature maps for North Macedonia with probability of occurrence of 0,002% (Source: Climate maps, UHMR, 2020)

The average annual precipitation in Kumanovo is 549.3 mm, making it one of the driest areas in Macedonia, while the surrounding mountainous region receives higher average annual precipitation. In Kumanovo, there are also dry periods when the total annual precipitation drops below 300 mm. On average, the months with the highest precipitation are November (72 mm), May (66 mm), and June (65 mm), whereas the months with the least precipitation are August (33 mm), September (29 mm), and February (35 mm) [1].

The Kumanovo region is characterized by extreme windiness, with the northern wind being the most common, followed by northwestern and southern winds. The northern wind blows throughout the year, with an average frequency of 33.1 %, being most often observed in June, July, and January, and least frequently in March and May. This wind typically dominates for a larger portion of the year. The average monthly speed of the northern wind can vary, averaging 3.2 m/s annually, with a maximum speed reaching 26.5 m/s. The second most frequent wind is the northwestern wind, which mainly occurs from May to October, with less frequency in the remaining months. The average annual speed of the northwestern wind is lower, at 1.9 m/s [1].

## 2.3. Transportation and energy infrastructure

The road infrastructure in Kumanovo comprises 888 km of local roads, 99 km of state roads, and 370 km of regional roads, establishing it as one of the main crossroads in the country. The Kumanovo region connects to the rest of the country through several major road routes, particularly the state roads A1 (Skopje-Kumanovo-border with the Republic of Macedonia) and A2 (Kumanovo-Kriva Palanka-border with Bulgaria).

Additionally, there are two railway lines in the Northeastern Planning Region. One line is part of Corridor 8, which connects to Corridor 10 via the city of Kumanovo. There is also a 33 km railway line from Kumanovo to Beljakovce, which is currently not operational.

As of 2023, the municipality of Kumanovo has established a public transport line between Proevce and Bedinje [5].

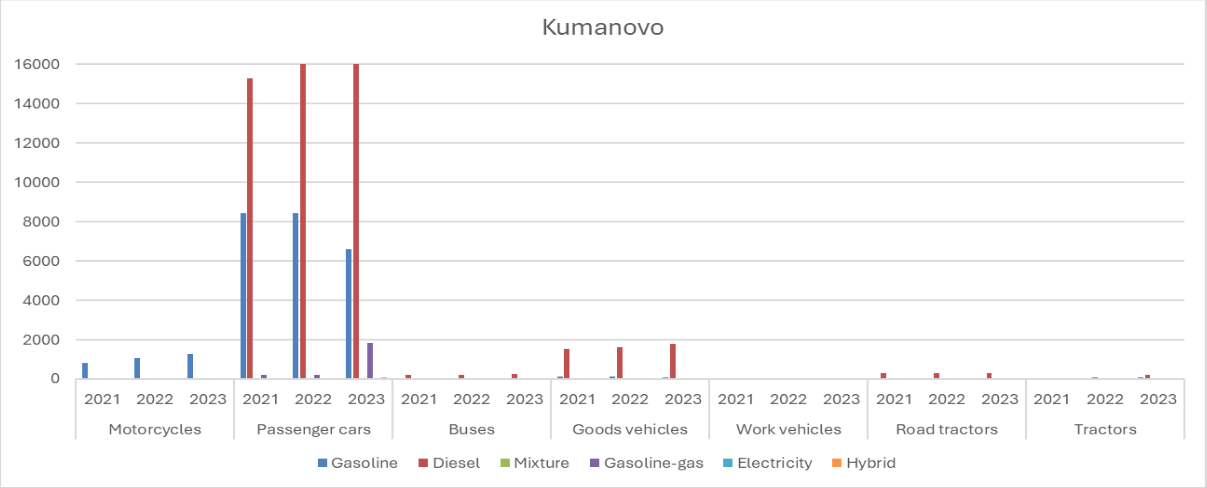


**Figure 5. Number of registered vehicles in Kumanovo classified according to the type and fuel used [4]**

In comparison to 2021, when 27,089 vehicles were registered, there were a record high of 30,049 vehicles registered in Kumanovo in 2023. The figure above presents the count of various vehicle types registered in Kumanovo from 2021 to 2023, along with the classification of the vehicle fleet based on the types of fuels utilized [4].

In the municipality of Kumanovo, there is no district heating system in operation, and all housing and public buildings utilize individual heating systems. According to the MAKSTAT database of the State Statistical Office, data on household energy consumption for 2019 indicate that firewood is the most commonly used source for heating households in the Northeast region.

Kumanovo is among the few urban areas that possess a developed and operational secondary gas pipeline infrastructure. This system connects to the transit gas pipeline that runs through Ukraine, Romania, and Bulgaria.

The secondary pipeline network extends 21 kilometres throughout the urban area of the city. This gas pipeline network links numerous public buildings, residences, and both service and industrial companies, yet its potential remains significantly underutilized [6].

## 2.4. Industry and service providers

The Pollutant Cadastre for the Municipality of Kumanovo identifies 209 stationary air emission sources, consisting of 117 non-production entities and 92 production entities.

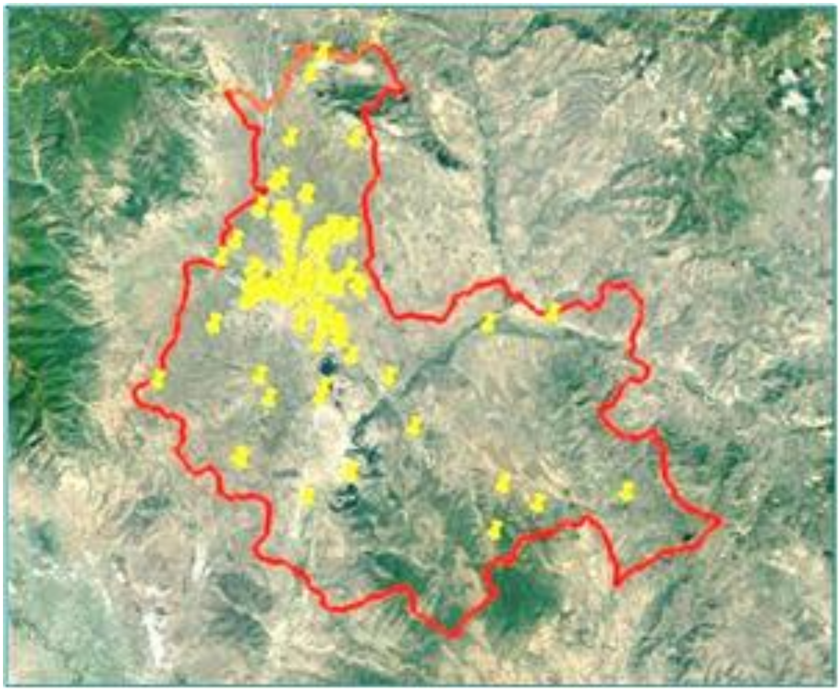


**Figure 6. Map of spatial distribution of business entities in the Municipality of Kumanovo [1]**

Non-production entities primarily consist of public buildings and service providers that typically operate small- to medium-sized boiler plants, mainly for heating purposes. These entities can significantly impact urban air quality, as many rely on outdated units powered by fuel oil, residual oil, or, in some cases, solid fuels such as lignite or wood.

Production facilities include small to medium-sized companies, predominantly from the food and beverage, construction, textile, and metal processing sectors.

Figure 7 illustrates the numbers of various types of production facilities and service providers located within the boundaries of the urban area.

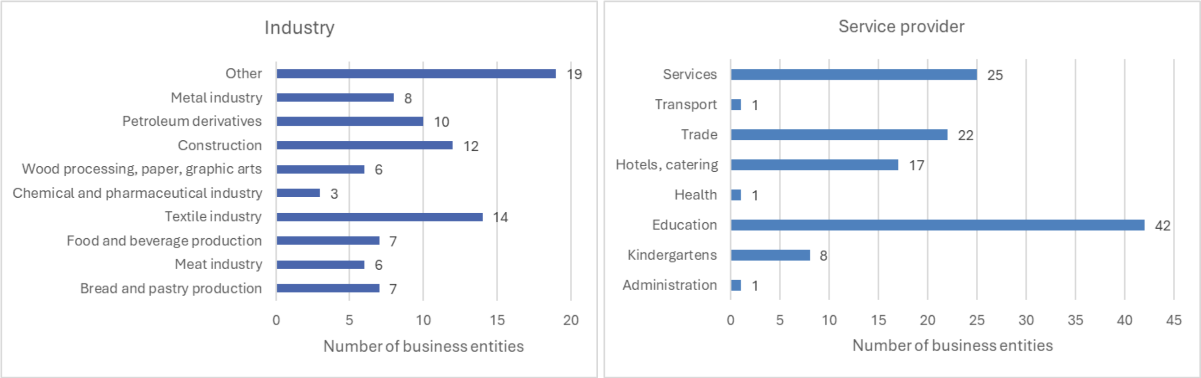


**Figure 7. Production business entities and service provider in the Municipality of Kumanovo by activity [1]**

## 2.5. Historical data on ambient air quality

The last assessment of ambient air quality was conducted as a part of the air quality improvement plan for Kumanovo Municipality [1], utilizing data sourced from the State Monitoring Network covering the years 2017 to 2021.

Data from the Kumanovo measurement station indicate that the average annual $SO_2$ values from 2017 to 2021 range between 1.65 and 2.70 $\mu g/m^3$, far below the regulatory limit of 20 $\mu g/m^3$ for ecosystem protection. No breaches of the hourly and daily $SO_2$ limits established for human health protection have been reported.

Figure 8. Average annual concentration of $SO_2$ from 2017 to 2021 [1]

Furthermore, the mean annual values of $NO_2$ were roughly 20 µg/m$^3$, much below the prescribed annual limit of 40 µg/m$^3$, and are therefore classified as a non-critical pollutant. During the specified timeframe, the hourly limit values defined for the protection of human health (fixed at 200 mg/m$^3$) were not exceeded.

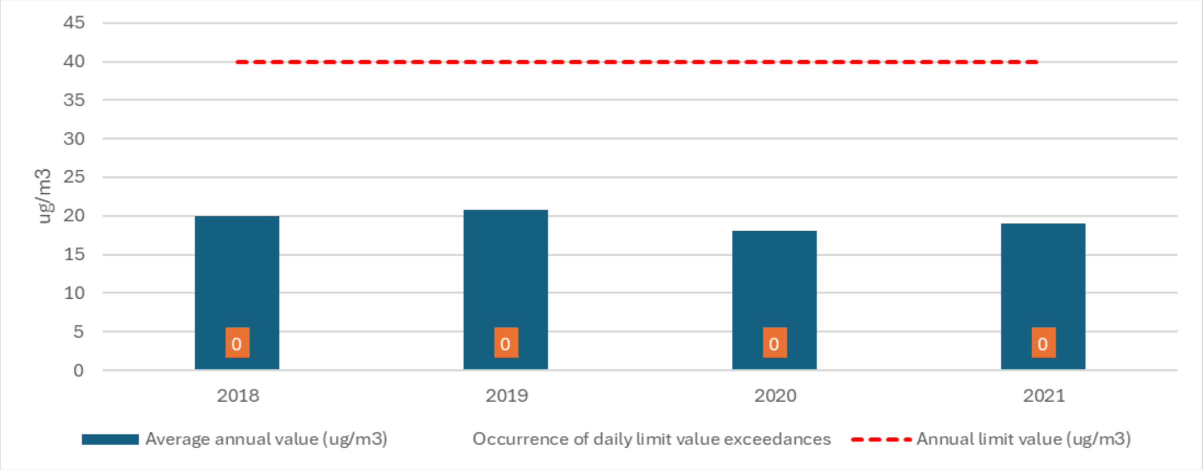


Figure 9. Average annual concentration of $NO_2$ from 2018 to 2021 [1]

Carbon monoxide (CO) concentrations fluctuated between 7 and 10.1 mg/m$^3$, nearing the threshold values; however, in 2018, there was a slight exceedance of the health protection target set at 10 mg/m$^3$.

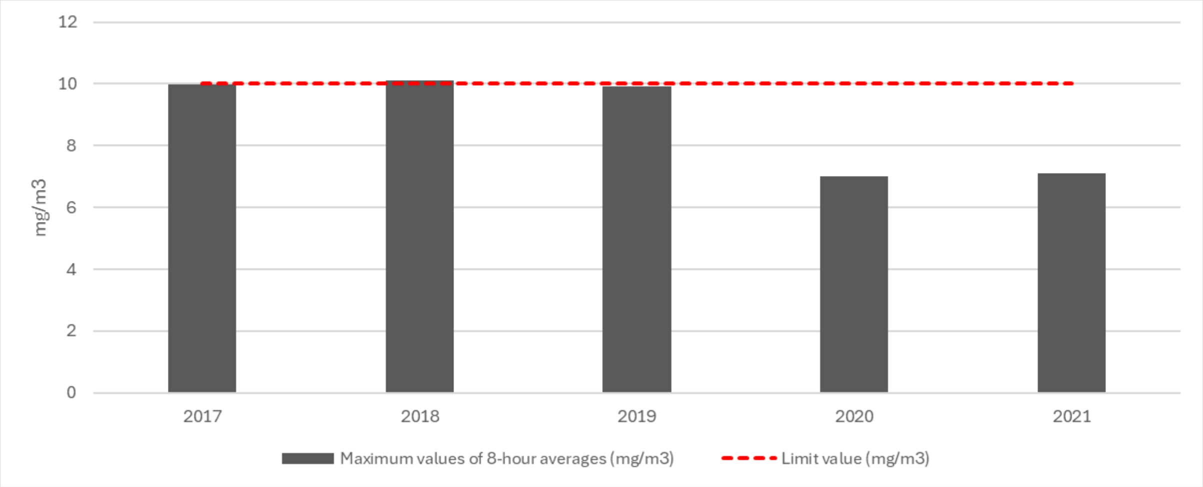


Figure 10. Maximum 8-hour averages of CO from 2017 to 2021 [1]

The ozone data spans from 102.82 to 126.68 µg/m$^3$, indicating that the human health protection threshold of 120 µg/m$^3$ was exceeded solely in 2021. Certain studies have indicated that ozone levels beneath these thresholds can still lead to increased mortality risks [7]. Studies have demonstrated the adverse effects of reduced ozone concentrations, as low as 40 ppb, on vegetation and agricultural crops [8, 9].

**Figure 11. Maximum 8-hour averages of $O_3$ from 2017 to 2021 [1]**

Nonetheless, particulate matter (PM 10) levels consistently exceed the prescribed threshold limits. The condition regarding suspended particulate matter is increasingly dire, as the frequency of exceeding the 24-hour limit and the average annual PM10 concentrations in Kumanovo from 2017 to 2021 consistently surpass the recommended standards.

Figure 12 illustrates that the annual total of 24-hour limit exceedances varies between 115 and 152, markedly exceeding the recommended threshold of 35 days. The annual limit for human health protection was consistently surpassed each year, with values ranging from 47 to 71 µg/m$^3$.

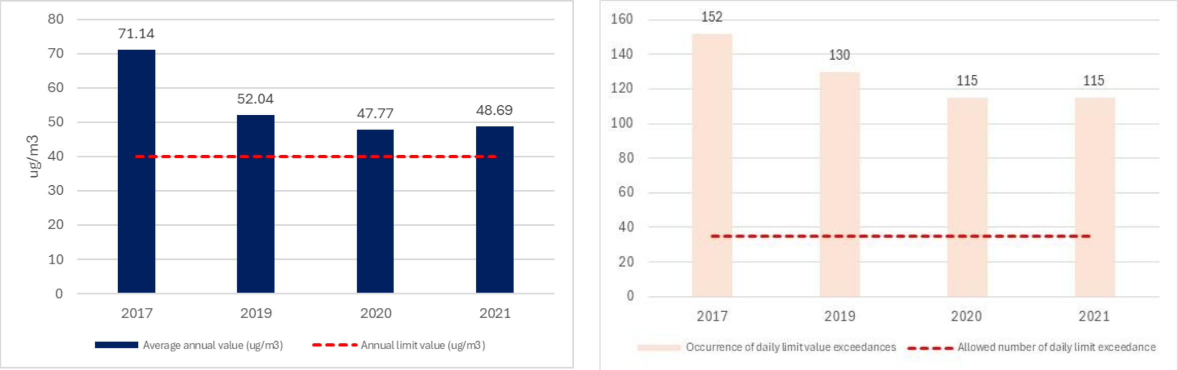


**Figure 12. Average annual PM10 concentrations and number of exceedances of the 24-hour limit value in Kumanovo from 2017 to 2021 [1]**

The fine particulate matter (PM 2.5) has been monitored since 2017; however, adequate data for evaluating annual averages is only available for 2018, 2020, and 2021.

The annual average concentrations for these three years have remained around 34 µg/m$^3$, which exceeds the recommended limit by approximately 38 %.

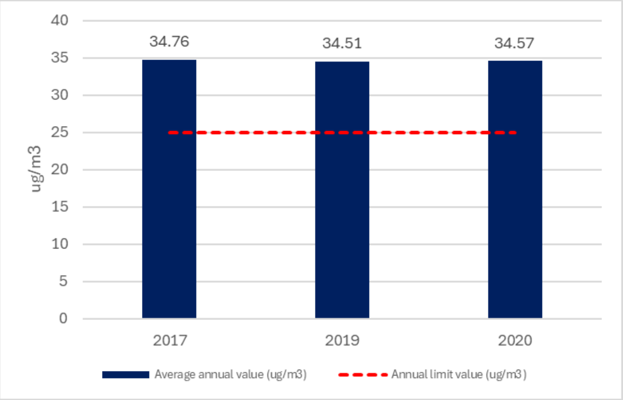


**Figure 13. Average annual PM2.5 concentrations in Kumanovo from 2017 to 2020 [1]**

# 3. Major emission sources

Emission data and corresponding source profiles were compiled using several relevant sources, including the Kumanovo Municipality Air Quality Improvement Plan for 2022-2026 [1], as well as the SPECIEUROPE repository [10], which contains chemical profiles of particulate matter obtained from source measurements conducted across Europe.

## 3.1. Emission inventory

The emissions inventory has been developed within the Air Quality Improvement Plan [1] by utilizing standardized approaches to estimate air pollutants and greenhouse gas (GHG) emissions across various sectors. Emissions inventories requires activity data (e.g., fuel consumption, industrial output) and emission factors that indicate quantity of pollutants released per unit of activity. Data sources commonly include industrial output reports, energy statistics, transportation statistics (vehicle types and usage, fuel consumption), agricultural activities and waste management data. In this particular instance, the primary data sources were official reports from IPPC installations (MOEPP) and the MAKSTAT database (State Statistical Office) [1].

Calculations conducted follow recommended procedures based on the:

- Intergovernmental Panel on Climate Change (IPCC) Guidelines for greenhouse gas emissions.
- European Environment Agency (EEA) EMEP/EEA Air Pollutant Emission Inventory Guidebook – pertaining to air pollutants [11].

Emissions were assessed using the Tier 1 or basic approach, utilizing default emission factors from international sources according to this formula:

Emissions = Activity Data x Emission Factor

where:

- Activity Data denotes the quantity of a particular activity (e.g., fuel consumed in tons).
- Emission Factor denotes emissions per unit of activity (e.g., kg of PM 2.5 per ton of fuel combusted).

In accordance with national regulations and guidelines (Nomenclature For Reporting - NFR and Guidelines for Drafting AQIP) [55], this inventory categorizes emissions into the following sectors: industry, transportation, public sector (administration and services), residential sector (households), industrial processes and products consumption, agriculture (which includes livestock and fertilizer usage), waste management (including emissions from landfills, wastewater treatment, and waste incineration) and natural sources.

The annual emissions of criteria pollutants have been calculated [1] and are detailed in Table 1.

**Table 1. Criteria pollutants emissions (in tons per year) for Kumanovo municipality [1]**

| | Pollutants (t/year) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Nox | CO | NMVOC | SOx | NH3 | TSP | PM10 | PM2.5 |
| Industrial process | 48.12 | 8.33 | 2.93 | 4.44 | 0.11 | 2.49 | 2.51 | 2.21 |
| Administrative facilities | 10.21 | 6.25 | 3.18 | 0.96 | 0.16 | 1.60 | 1.03 | 0.98 |
| Households | 28.40 | 2177.47 | 326.30 | 3.76 | 27.38 | 434.81 | 297.66 | 289.83 |
| Traffic | 514.23 | 710.86 | 147.63 | 0.87 | 6.59 | / | / | 35.43 |
| Waste | 2.11 | 37.09 | 389.96 | 0.07 | / | 30.91 | 30.05 | 27.81 |
| Agriculture | 32.98 | / | 83.38 | / | 238.41 | 31.10 | 9.78 | 3.90 |

As illustrated in Fig. 14, household heating are the predominant sources of particulate matter emissions, with 87 % of PM10 emissions and 80 % of PM2.5 emissions.

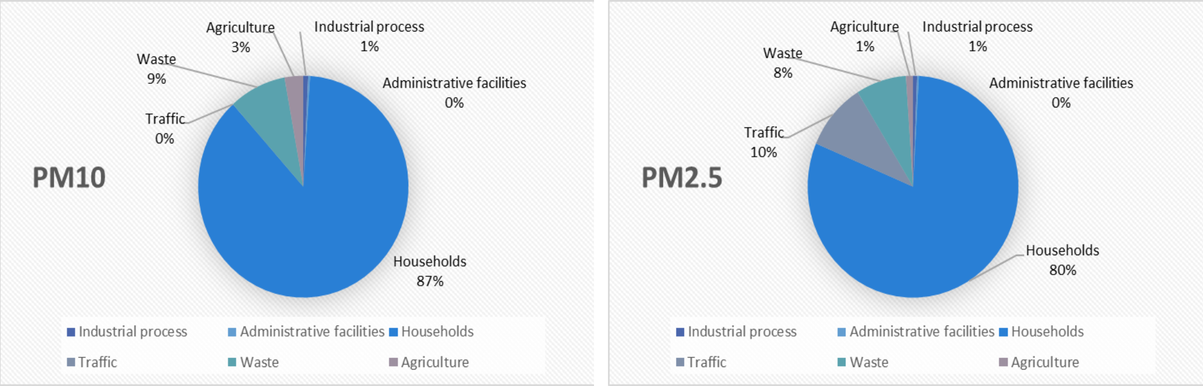


**Figure 14. Sectoral contribution to particulate mater emissions**

## 3.2. Source profiles

Chemical profiles of the sources identified in the inventory were obtained using the data published in SPECIEUROPE, a repository of source profiles developed by the JRC in the framework of FAIRMODE project [13]. SPECIEUROPE comprises chemical profiles of particulate matter, both organic and inorganic, derived from measurements of European sources and source apportionment investigations conducted in Europe.

Based on data given in the emission inventories, chemical profiles for following sources are included:

- Woodstove burning
- Open burning of crop residues
- Construction
- Traffic urban + Vehicle Exhaust
- Soil dust + Road dust
- De-icing Salt
- Fuel oil + Residual oil

A brief description of the source, sampling and analytical procedures that were employed, geographical location, elemental composition (relative mass of the elements), and bibliography are provided in the sections that follow.

Woodstove burning profile is based on JRC data, referencing closed fireplace wood combustion in Krakow, Poland. Elemental analysis was performed using particle induced x-ray emission (PIXE), photometric and ion chromatography (IC) methods are used for water soluble ions analysis, thermal optical analysis (TOT) was used for OC and EC analysis, and gas chromatography-mass spectrometry (GC-MS) for organic compounds. Organic carbon (OC) and elemental carbon (EC) are by far most abundant compounds (89.63 and 6.65 % respectively), followed by K (1.11 %) and Cl (0,43 %). Sulphates (0.87 %) and nitrates (0.25 %) are most abundant ions.

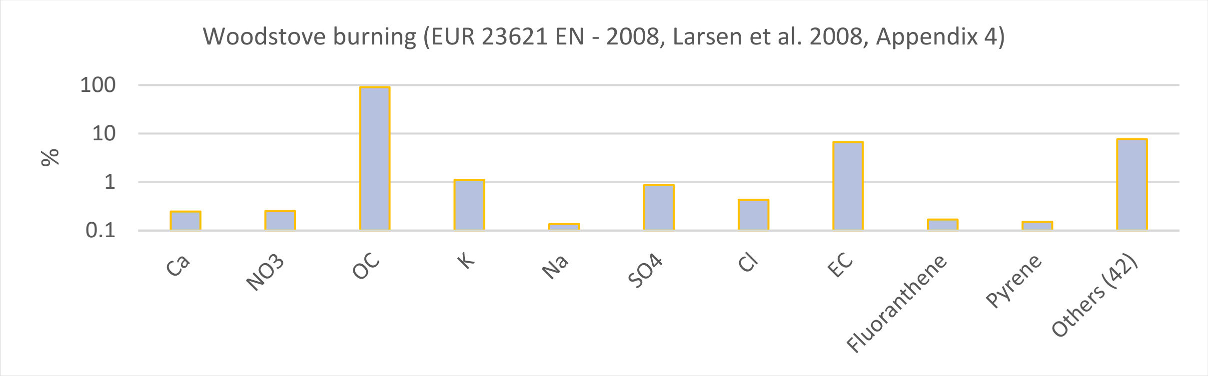


**Figure 15. Woodstove burning chemical profile (closed fireplace)**

Open burning of crop residues, or agricultural fields burning profile is based on direct on filter samples from Thessaloniki area in Northern Greece. Samples were analysed using energy dispersive X-ray fluorescence (ED-XRF) for elemental composition and ion chromatography (IC) for water soluble ions analysis. Bromine is most abundant element (9.43 %), followed by EC (9.0%) and Co (9,0 %). Other metals including V (8.133 %), Ti (4.83 %) and As (1.1 %) also have significant concentrations. Sulphates (8.13 %) are by far most abundant ion.

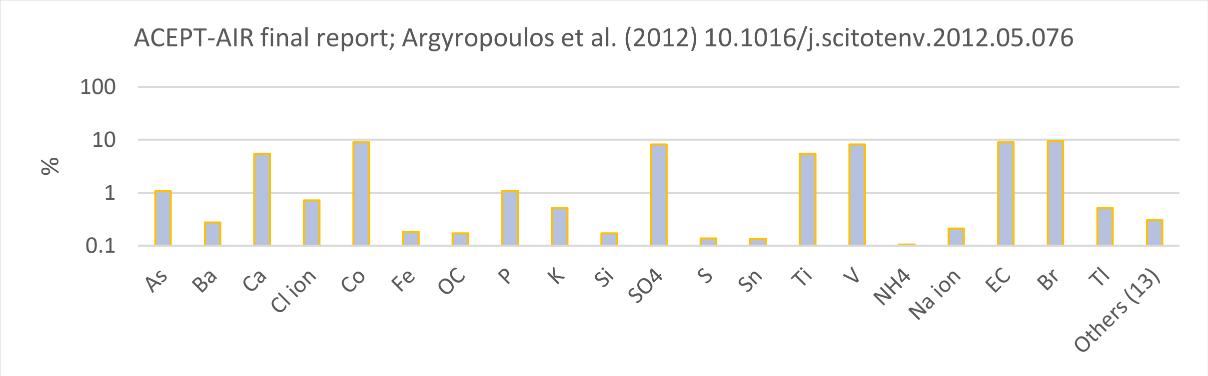


**Figure 16. Open burning of crop residues chemical profile**

Construction activities source profile is based on data obtained from Milan, Italy. Specific information's about sampling and analytical procedures used, were not provided. Calcium is most abundant element (19.85 %), closely followed by OC (17.9 %) and Si (12,55 %). Other metals including Ni (7,66 %), Al (3.78 %), Fe (1.91 %) and K (1.71 %) also have significant concentrations. Sulphates (9.14 %) and ammonium (1.96 %) are most abundant ions.

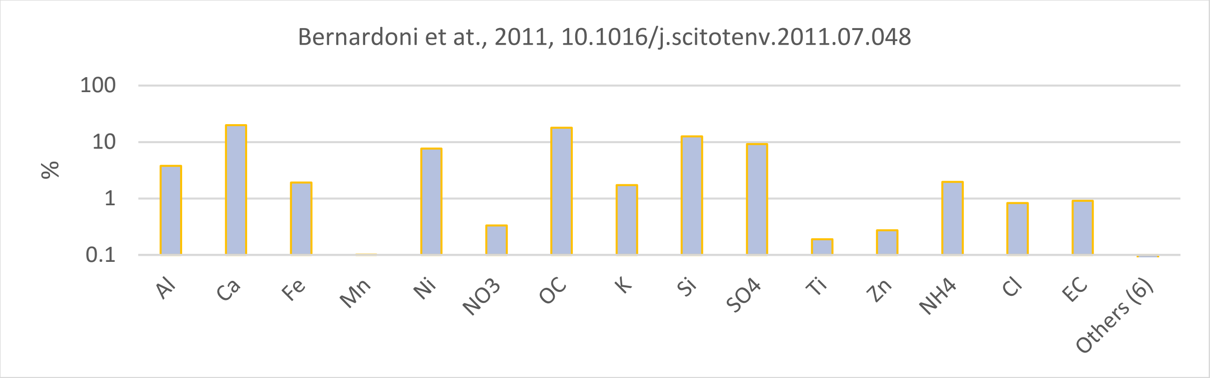


Figure 17. Construction activities chemical profile

Traffic source profile include two separate profiles, exhaust diesel and gasoline and urban traffic profile, based on data from PMF exercises in Valtellina, Po Valley, and Genoa Corso, Firenze in Italy. Specific information's about sampling and analytical procedures used, were not provided. OC and EC are most abundant compounds in both profiles, OC (53.59 and 35.1 %) and EC (30.46 and 23.04 %) respectively. Some metals including Fe (13.56 and 2.34%), Cu (1.1%) and Si (0.89%) in mixed exhaust and Ca (1.89 %) in urban traffic mix, also have significant concentrations. Sulphates (5.05 %) are by far most abundant ion in mixed exhaust, while ammonium (1.68 %) and nitrates (1.51 %) are most abundant ions in urban traffic mix.

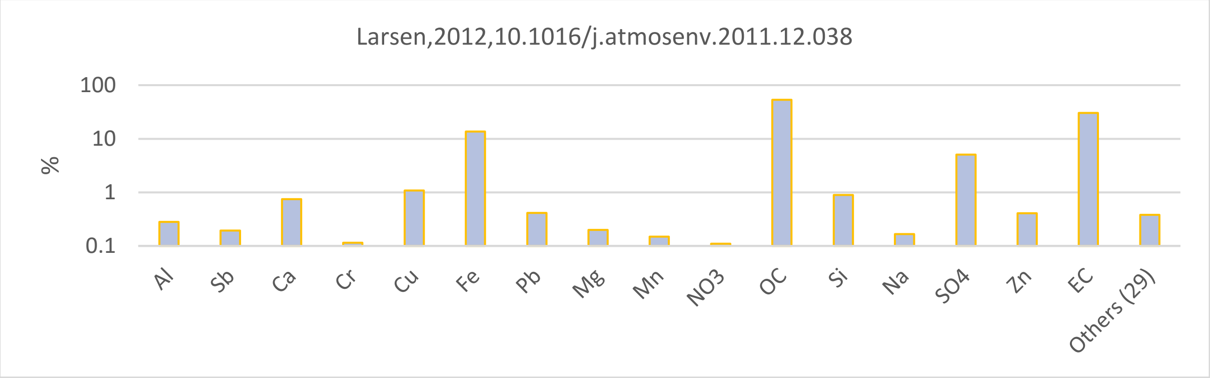


Figure 18. Exhaust diesel and gasoline chemical profile

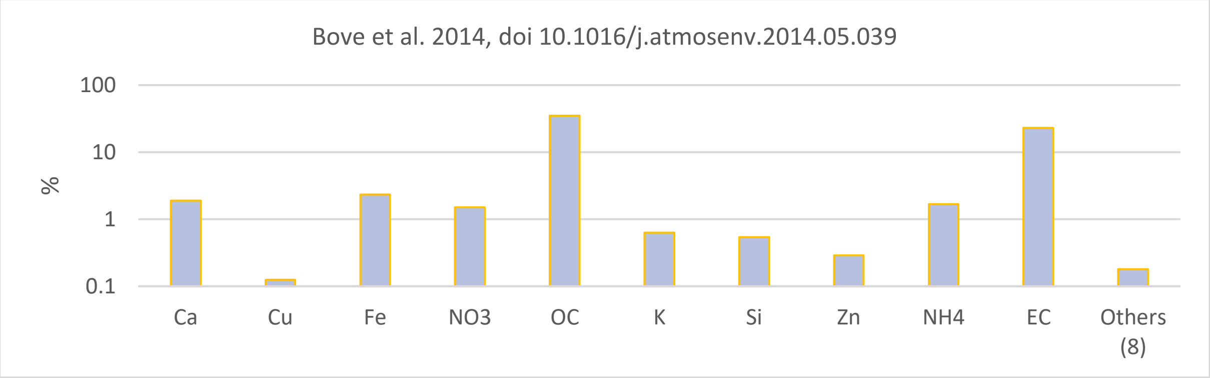


Figure 19. Urban traffic chemical profile

Road dust is another profile associated with traffic emissions. The profile selected is based on data from PMF exercises in Valtellina, Po Valley in Italy. Description of sampling and analytical procedures used, was not included. Silica is most abundant elements (15.63 %), followed from OC (7.25 %), Al (7,07 %), Fe (4.19 %), Ca (2.41 %), Mg (1.37%) and K (1.43 %). No significant concentrations of water-soluble ions were reported.

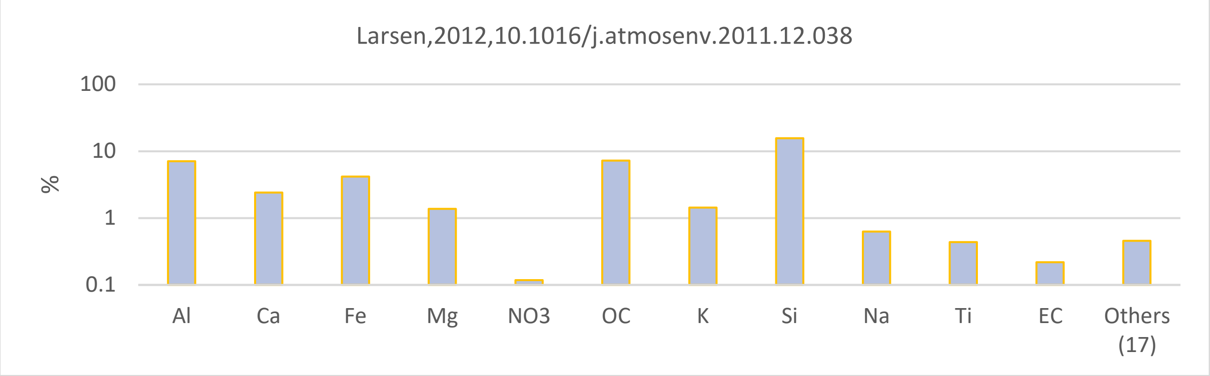


Figure 20. Road dust chemical profile

Soil dust profile is based on grab dust samples collected from the fabric filter from Thessaloniki area in Northern Greece. Samples were dried and resuspended in a puff of clen air, then sampled with PM10 inlet with LVS, and analysed using energy dispersive X-ray fluorescence (ED-XRF) for elemental composition and ion chromatography (IC) for water soluble ions analysis. Silica is most abundant element (20.9 %), followed by Al (5.65 %), Fe (4,36 %), Ca (3.20 %), Mg (1.56 %), K (1.37 %) and Ti (0.41 %). No significant concentrations of water-soluble ions were reported.

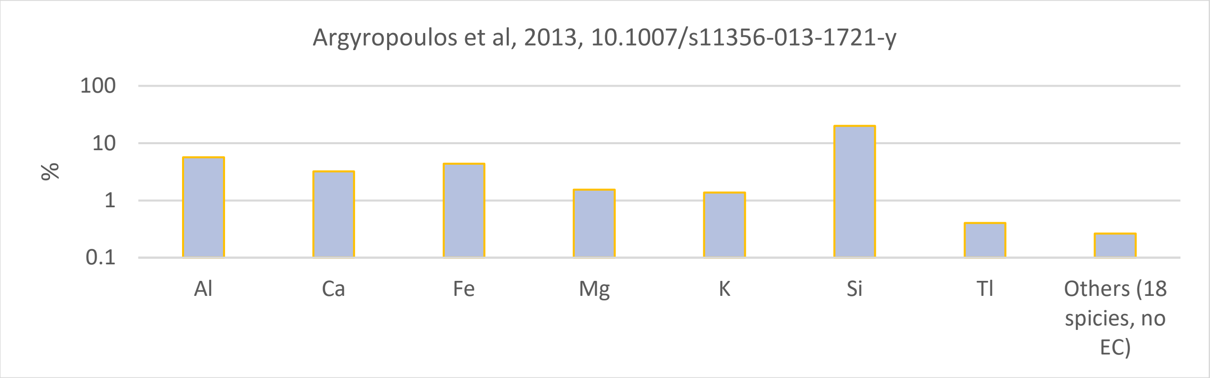


Figure 21. Soil dust chemical profile

Fuel and residual oils burning includes emissions from a wide range of sources, the majority of which are larger buildings heating systems (schools, hospitals, and other public institutions), industrial combustion emissions and to some extent older diesel-powered vehicles emissions.

Residual oil chemical profile is based on data from PMF exercise in Genoa Corso, Firenze in Italy. Samples were analysed using energy dispersive X-ray fluorescence (ED-XRF) for elemental composition, ion chromatography (IC) for water soluble ions analysis, and thermal optical analysis (TOT) for OC\EC analysis. Elemental carbon is by far most abundant compound (31.3%), followed by sulphates and ammonium ions (23 and 5.75 % respectively). As of metals, iron and vanadium exhibit highest concentrations (0.98 and 0.76 % respectively), followed by Ni (0.28 %), K (0.128 %) and Ca (0.10 %).

Fuel oil chemical profile is based on JRC data on small (<5MW) fuel oil boilers emission in Krakow, Poland. Specific information's about sampling and analytical procedures used, were not provided. Organic carbon is most abundant compound (25.3 %), followed by nitrates (18.53 %) and sulphates (13.78 %). Other elements include Ca (1.2 %), Cl (1.16 %), Mg (0.57 %), Al (0.42%), V (0.16 %) and Ni (0.14 %).

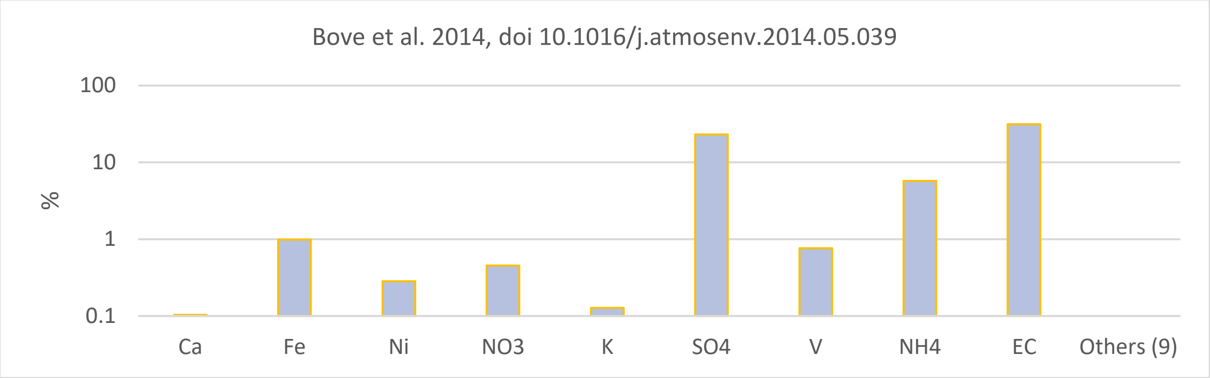


**Figure 22. Residual oil chemical profile**

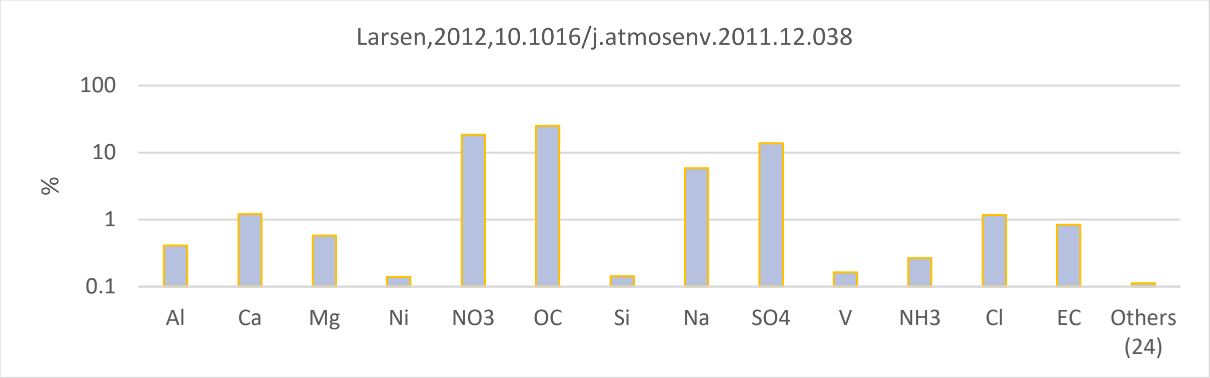


**Figure 23. Fuel oil chemical profile**

The source profiles outlined above were utilized to assign source categories to factors generated during positive matrix factorization. This procedure was supported with quantitative and descriptive comparison of the factor chemical profiles with those measured at the source and profiles from previous source apportionment studies in the literature, as given above.

# 4. Particulate matter sampling and analysis

Given the goals of the SA study, the available data, and the project document needs, we chose and set up one specific receptor/sampling point in the urban areas of Kumanovo.

The sampling site in Kumanovo (our code MP3 – AQP) is situated in close proximity to an automated state monitoring station, which is positioned near the hospital and adjacent to the main entrance route to the city. The road is around 35 meters away, while the highway is situated at a distance of 600 meters. Measured concentrations are not significantly affected by input from local industry sources.

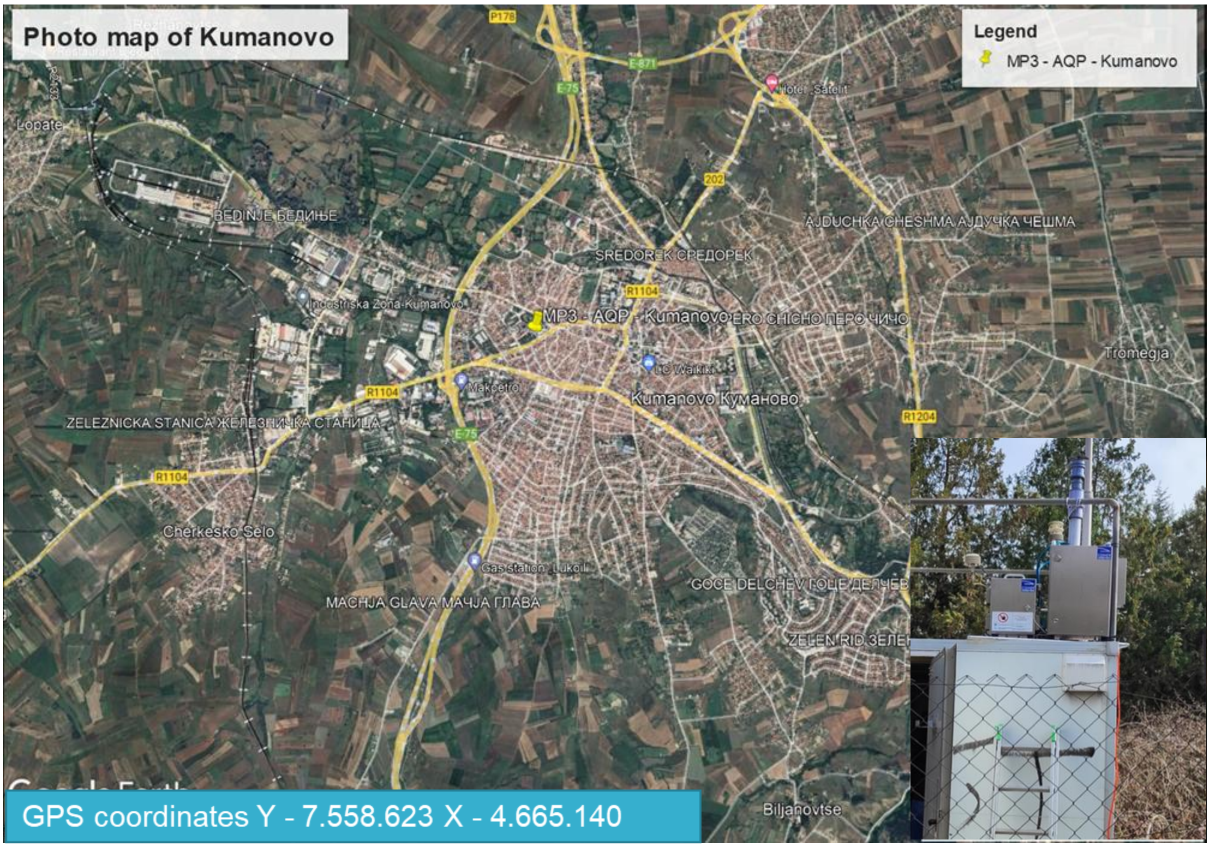


**Figure 24. Monitoring location in Kumanovo urban area**

The sampling program at this site commenced on March 10, 2023. A 24-hour sample was collected every other day, resulting in a total of 173 samples by March 25, 2024.

All quality assurance and quality control procedures for preparing, handling, and storing the filters were conducted in accordance with the Standard Operating Procedure of the UGD AMBICON Lab, which is certified to ISO 17025 for environmental sampling and testing.

## 4.1. Sampling and determination of mass concentration of ambient particulate matter (PM2.5)

Sampling process was performed fully in line with the requirements of standard gravimetric measurement method for determination of the PM10/PM2,5 mass concentration of suspended particulate matter (EN 12341:2014). Sampling was performed on 47 mm PTFE filters (Advantec depth filter PF 020 and PF 040), according to Standard Operating Procedure of the UGD AMBICON Lab, an ISO 17025 accredited for environment and samples from the environment testing (https://iarm.gov.mk/en/2021/07/01/lt-052-university-goce-delcev-shtip/).

### Sampling procedure

The sampling site was equipped with low/medium volume sequential sampling system (PNS 18T-DM-6.1, Comde Derenda, Germany), certified as a reference device for PM2.5 sampling according to EN 12341:2014.

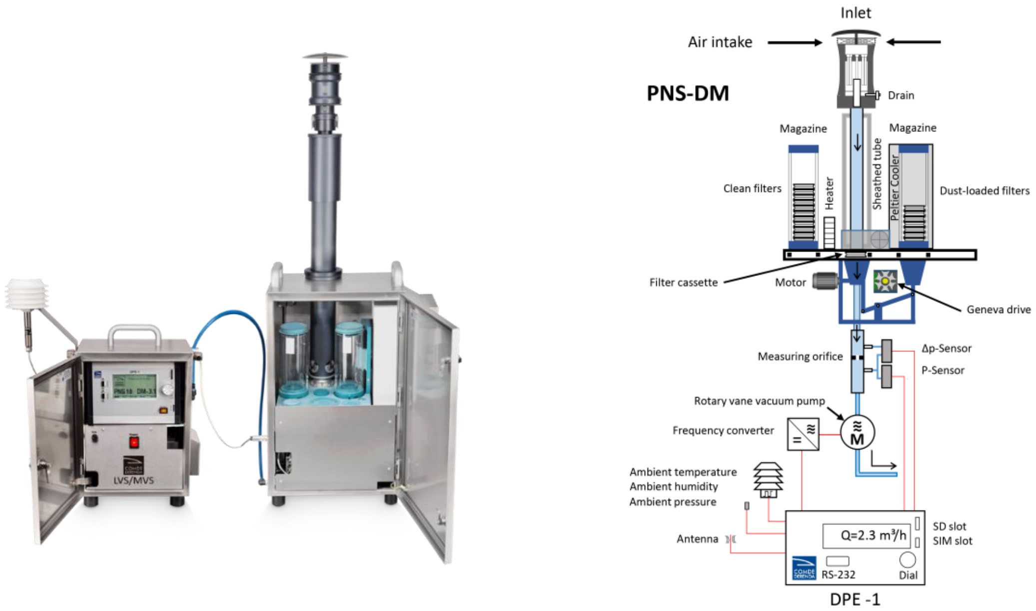


**Figure 25. Sequential sampling system PNS 18T-DM 6.1**

Sequential sampling systems provide fully automatic sampling according to pre-set parameters. Session from 14 to 16 days were set for each site. Each initial magazine was loaded in the AMBICON Lab premises with 16 to 18 filters, of which top one was not used for sampling, but as a protection in order to collect possible passive particle deposits. Additional one was transferred to the storage magazine without exposure and used as a field blank.

All monitoring data were electronically recorded, including sample ID, pump runtime, time of measurement, motor speed, actual flow, normalized flow, volume sampled-actual, volume sampled-normalized, filter pressure, ambient air pressure, outdoor temp, filter temp, chamber temp and relative humidity.

During each filter magazine change operation or at a period of 14 to 16 days, several quality assurance and control procedures were performed, including:

- sampling head cleaning,
- reading accuracy check for all sensors, and
- leak tightness test.

Sampling head, including inside of the tubular casing, the intake side of the multijet unit, the impaction plate and the jet tubes will be cleaned with alcohol and wiped with dry cloth. Impaction plate will be greased with silicone spray lubricant. The insect screen will be checked for obstructions and cleaned if necessary. Notes about cleaning and visual inspection were recorded in lab sampling logbook.

Reading accuracy of all sensors was checked through a short sampling test cycle, all the while, readings of the sensors was compared against external calibrated standards, including:

- test of flow rate set, against the reading of calibrated external flow meter (with certificate issued from ISO 17025 calibration lab),
- test of system temperature, humidity and ambient pressure readings, against calibrated external ambient Temp and RH meter (with certificate issued from ISO 17025 calibration lab),

Data about readings from all sensors were recorded in separate form of lab sampling logbook.

Leak tightness test of the system was performed through a low-pressure method, fully according to section 5.1.7.2 of the EN 12431:2014. The system has integrated leak test procedure, where pump is run, with closed calibration adapter until 400 hPa under-pressure in chamber is reached. The pump is switched of, and after 5 minutes pressure is read from the screen. If the value of under-pressure in the chamber is above 210 hPa, the system has passed the run test. According to above norm requirements, the test was repeated 3 times (total 3 runs). Data from the test runs were recorded in separate sheet of lab sampling logbook.

### Filters handling and weighing

Prior to sampling, all filters were uniquely identified and conditioned at 19 °C to 21 °C and 45 to 50 % RH in climate chamber (ICH 110, Memmert, Germany) for ≥ 48 h, and weighted twice with at least 12 hours reconditioning period, to confirm mass stabilization (qualified difference < 40 µg). For each batch, two (2) blank filters are left to serve as a weighing room blanks.

Figure 26. Weighing room- AMBICON UGD Lab

After each sampling session, storage and initial magazine were removed from the housing. Protective reference filter was removed from the magazine and discarded, while empty magazine was fixed as new storage magazine. As soon as removed from the housing, storage magazine was sealed with cap and parafilm and stored in transportation “cool box”.

Sampled filters after exposure were returned to the weighing room and conditioned in a controlled temperature and humidity chamber for more than 48 hours and weighted. After additional conditioning period of minimum 24 hours, filters were re-weighted and accepted as stabilized if difference between results is ≤ 60 µg. Same conditions was applied for filed blanks.

Weighing was performed with electronically controlled micro balance Radwag MYA5.3Y.F (resolution d = 1 µg), installed within controlled temperature and humidity room and completed with antistatic ionizer. Weighing data set and room conditions were electronically recorded.

Ongoing quality control were performed fully in line with the requirements of standard gravimetric measurement method for determination of the PM10/PM2,5 mass concentration of suspended particulate matter (EN 12341:2014), according to standard operating procedure of UGD AMBICON Lab, an ISO 17025 accredited for environment and samples from the environment testing areas.

Measurement uncertainties were calculated following GUM concept (JCGM 100) and included all individual uncertainty sources.

Mass concentration of ambient particulate matter was calculated as the difference in mass between the sampled and unsampled filter, divided by the sampled volume of air, determined as the flow rate multiplied by the sampling time. Measurement results are expressed as µg/m$^3$, where the volume of air is that at the ambient conditions near the inlet during sampling.

Data collected and comments are included in each filter testing results, given as supplementary material to this report (A – 1 Mass concentration of ambient particulate matter).

## 4.2. Chemical speciation

The elemental analysis of collected atmospheric aerosols (PM2.5) is the initial step in determining their sources and environmental impact. It can be accomplished by several methods. Certain analytical procedures are prohibitively expensive, others are labor-intensive, and some approaches result in sample destruction. This study utilized energy dispersive X-ray fluorescence (ED-XRF) for elemental composition analysis, optical transmissometer for measuring elemental carbon content, and spectrophotometry for the detection of water-soluble ions.

### Elemental analysis using energy dispersive X-ray fluorescence spectrometry

The elemental analysis of PM2.5 of aerosols was conducted using energy dispersive X-ray fluorescence spectrometer NEX CG produced by Rigaku. The secondary targets of the NEX CG substantially improve detection limits for elements in highly scattering matrices including water, hydrocarbons, and biological materials, and a unique close-coupled Cartesian Geometry optical kernel significantly increases signal-to-noise. The spectrometer is capable of routine trace element analysis even in filter samples, thanks to the remarkable reduction in background noise and corresponding increase in element peaks [13].

Figure 27. NEX CG by Rigaku

Analyses were carried out in the AMBICON Lab, at Goce Delcev University in Stip, North Macedonia, according to the EPA/625/R-96/010a Compendium of Methods, Method IO-3.3: determination of metals in ambient particulate matter using x-ray fluorescence (XRF) spectroscopy published by U.S. Environmental Protection Agency.

The calibration curve on the NEX CG was generated utilizing certified standard reference materials from UC Davis, Air Quality Research Center, University of California (USA), alongside SRM2783 from the National Institute of Standards and Technology (USA) and select single element certified reference materials from Micromatter (Canada). The calibration primarily utilized three multi-element reference materials, encompassing 28 components, which simulated atmospheric PM composition and covered a range from UC Davis. In addition to these three loaded filters, one UC Davis blank filter was also utilized.

Alongside continuous quality control and weekly monitoring of the certified reference filters (Table 2), we also ensure quality through inter-laboratory comparisons (Table 3).

**Table 2. Quality control results of EDXRF NEX CG by Rigaku**

| Element | Certified reference concentration (ng/cm$^2$) | Average | Standard deviation | Coefficient of variation (%) | Recovery (%) |
|---|---|---|---|---|---|
| Na | 178.43 | 149.76 | 31.18 | 20.82 | 100.0 |
| Mg | 89.84 | 89.11 | 3.88 | 4.36 | 100.0 |
| Al | 376.00 | 373.29 | 11.40 | 3.05 | 100.0 |
| Si | 1168.57 | 1159.05 | 21.19 | 1.83 | 100.0 |
| P | 9.17 | 9.09 | 0.27 | 2.95 | 100.0 |
| S | 1644.29 | 1644.29 | 46.11 | 2.80 | 100.0 |
| K | 2628.57 | 2640.00 | 25.50 | 0.97 | 100.0 |
| Ca | 3622.86 | 3623.81 | 22.91 | 0.63 | 100.0 |
| V | 8.20 | 8.17 | 1.13 | 13.81 | 100.0 |
| Cr | 81.00 | 82.80 | 2.12 | 2.56 | 100.0 |
| Mn | 24.99 | 26.66 | 3.00 | 11.27 | 100.0 |

| Element | Certified reference concentration (ng/cm$^2$) | Average | Standard deviation | Coefficient of variation (%) | Recovery (%) |
|---|---|---|---|---|---|
| Fe | 733.14 | 728.86 | 14.74 | 2.02 | 100.0 |
| Co | 37.43 | 41.63 | 5.24 | 12.59 | 100.0 |
| Ni | 60.00 | 64.76 | 5.03 | 7.76 | 100.0 |
| Cu | 26.50 | 28.15 | 5.70 | 20.23 | 100.0 |
| Zn | 103.30 | 105.21 | 5.57 | 5.30 | 100.0 |
| As | 142.17 | 151.95 | 25.94 | 17.07 | 100.0 |
| Se | 88.00 | 89.06 | 5.35 | 6.01 | 100.0 |
| Zr | 20.50 | 21.17 | 1.04 | 4.92 | 100.0 |
| Mo | 18.79 | 18.80 | 0.53 | 2.81 | 100.0 |
| Cd | 440.71 | 482.71 | 48.49 | 10.05 | 100.0 |
| Ba | 75.29 | 74.83 | 4.54 | 6.07 | 100.0 |
| Pb | 210.00 | 195.13 | 15.68 | 8.04 | 100.0 |

The inter-laboratory comparison was conducted directly between AMBICON Lab and the Institute of Nuclear & Radiological Sciences and Technology, Energy & Safety (INRASTES), affiliated with the National Center for Scientific Research Demokritos in Greece. A comprehensive comparison was performed using 21 PTFE filters with different loadings, comprising 20 samples and 1 blank.

The findings from the calculated Zeta-score have been considered acceptable, as presented in Table 3.

**Table 3. Zeta-score results of EDXRF inter-laboratory comparison**

| Element | Zeta Score | Element | Zeta Score | Comments/Notes |
|---|---|---|---|---|
| Na | 1.68 | Ni | 0.34 | Explanation of Zeta-score values:<br>$\lvert z \rvert \le 2.0$ the result is considered acceptable<br>$2.0 < \lvert z \rvert < 3.0$ indicate a warning signal<br>$\lvert z \rvert \ge 3.0$ results are considered unacceptable |
| Mg | 1.21 | Cu | 2.31 | |
| Al | 1.69 | Zn | 0.80 | |
| Si | 1.34 | S | 0,41 | |
| Mn | 1.04 | K | 0,67 | |
| Fe | 0.80 | Ca | 1.34 | |
| Cr | 0.39 | Ba | 2.49 | |
| Pb | 1.09 | | | |

## Analysis of water-soluble ions

Water-soluble ions were extracted from the aerosol filters using sonication and shaking as recommended in the in-house developed Standard Operating Procedure for PM2.5 Cation Analysis [14]. The filters were cut in half using ceramic scissors and the mass of the filters was determined using electronically controlled micro balance with resolution of 1 µg. Half of the filter is placed in plastic centrifuge tubes filled with 25 mL ultra-pure water (> 18MΩ-cm) and sonicated on room temperature in the ultrasonic bath (GT Sonic Pro, UK) for 60 minutes. Ice was added in the ultrasonic bath to keep the temperature below 27$^0$C. After the sonication, the centrifuge tubes were shaken for 9 hours at 640 rpm using IKA KS 130 orbital shaker. After the procedure is completed, and in order to provide time for sample stabilization, the samples were stored in refrigerator overnight.

Water-soluble ions, including sulphates ($SO_4^{2-}$), nitrates ($NO_3^-$) and ammonium ($NH_4^+$) have been measured photometrically using the Spectroquant® Prove 600 spectrophotometer by Merck.

Figure 28. Spectroquant® Prove 600, Merck

Ammonium ions were analyzed using 1.14752.0001 Spectroquant® cell test analogous to EPA 350.1, ISO 7150-1 and DIN 38406-5 methods and detection limit of 0.015 mg/l $NH_4^+$. Quality control was provided using Certipur - certified reference solution of $NH_4Cl$ in $H_2O$ (1000 mg/l $NH_4^+$) traceable to NIST.

The sulphate ions were analyzed using 1.01812.0001 Spectroquant® cell test analogous to EPA 375.4, APHA 4500-$SO_4^{2-}$E, and ASTM D516-16 methods and detection limit of 0.5 mg/l $SO_4^{2-}$. Quality control was provided using Certipur - certified reference solution of $Na_2SO_4$ in $H_2O$ (1000 mg/l $SO_4$) traceable to NIST.

Nitrate ions were analyzed using 1.09713.0001 Spectroquant® cell test analogous to DIN 38405-9in method and detection limit of 0.2 mg/l $NO_3^-$. Quality control was provided using Certipur - certified reference solution of $NaNO_3$ in $H_2O$ (1000 mg/l $NO_3^-$) traceable to NIST.

Table 4. Quality control results for water soluble ions standard operating procedure

| Ion | Concentration in certified reference solution | | Average | Standard deviation | Coefficient of variation (%) | Recovery (%) |
|---|---|---|---|---|---|---|
| | mg/l | Certified reference solution | | | | |
| $NH_4^+$ | 0.1 | $NH_4Cl$ in $H_2O$ (1000 mg/l $NH_4^+$), Certipur | 0,10 | 0,02 | 19,81 | 100.0 |
| $SO_4^{2-}$ | 10 | $Na_2SO_4$ in $H_2O$ (1000 mg/l $SO_4$), Certipur | 10,31 | 0,70 | 6,76 | 100.0 |
| $NO_3^-$ | 10 | $NaNO_3$ in $H_2O$ (1000 mg/l $NO_3^-$), Certipur | 9,64 | 0,61 | 6,33 | 100.0 |

## Elemental Carbon analysis

Black Carbon or Elemental Carbon was determined using Magee Scientific, SootScan™ Model OT21 Optical Transmissometer with dual wavelength light source (880nm providing the quantitative measurement of Elemental Carbon in PM, and a 370 nm for qualitative assessment of certain aromatic organic compounds), by applying EPA empirical EC relation for Teflon FRM filters.

**Figure 29. Magee Scientific, SootScan™ Model OT21 Optical Transmissometer**

The reproducibility of the photometric detector is validated using a Neutral Density Optical Kit, which is traceable to NIST and recommended by the manufacturer.

## 4.3. Observations and results

This sections present observations from the monitoring program conducted in Kumanovo, staring from March 2023 and ending March 2024. Results present daily variations in mass concentrations and chemical composition of PM with respect to various chemical species including carbon fraction (Elemental Carbon), crustal elements (Al, Si, Ca, Ti and Fe), water soluble ions ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$ ) and larger group of other elements (Na, Mg, P, S, Cl, K, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Ba, Pb).

### Statistical Evaluation

Descriptive statistics help us summarize, describe, and illustrate the data in a more meaningful fashion, making data interpretation easier. Therefore, we provide a summary of descriptive coefficients for each of the sites included in the monitoring program below.

The descriptive statistical analysis presented includes both categories: measures of central tendency and measures of variability (or variation).

Measures of central tendency are techniques for describing the position of the center of a frequency distribution for a given set of data. Although numerous statistics such as the mode, median, and mean can be used for this purpose, the middle position in this case is represented by the arithmetic mean.

Measures of variability provide a summary of a data set by illustrating the distribution of the observed results. Several statistics to explain this spread are utilized, including minimum, maximum, quartiles, variance, and standard deviation. Descriptive coefficients are combined with tabular and graphical descriptions, along with comments and discussions of the results.

Additionally, a correlation matrix illustrating the relationship between all values in the dataset is provided as a basic tool for summarizing large datasets and identifying and visualizing data relationships.

The correlation matrix table contains the correlation coefficients between each variable based on the Pearson parametric correlation test and is color-coded for correlation values above ± 0.6. In this case, correlation matrices show how the species are related, pointing out their shared sources, and they are also used for exploratory factor analysis and checking data quality.

**Table 5. Statistical evaluation – Kumanovo dataset**

| | Units | N | Mean | SD | Minimum | Maximum | C.V. | 95 th % | 5 th % |
|---|---|---|---|---|---|---|---|---|---|
| PM2,5 | µg/m$^3$ | 173.0 | 38.5 | 31.7 | 7.4 | 214.9 | 82.4 | 101.6 | 12.2 |
| Na | ng/m$^3$ | 173.0 | 16.7 | 36.1 | 5.5 | 265.9 | 216.5 | 70.3 | 5.5 |
| Mg | | 173.0 | 14.9 | 18.6 | 0.7 | 170.1 | 125.0 | 41.6 | 0.7 |
| Al | | 173.0 | 78.1 | 81.3 | 0.5 | 577.0 | 104.2 | 223.0 | 4.4 |
| Si | | 173.0 | 258.4 | 246.5 | 0.4 | 1784.6 | 95.4 | 674.2 | 32.6 |
| P | | 173.0 | 1.7 | 1.2 | 0.0 | 9.1 | 68.6 | 3.6 | 0.1 |
| S | | 173.0 | 153.2 | 134.4 | 0.2 | 1156.9 | 87.7 | 329.5 | 24.6 |
| Cl | | 173.0 | 39.5 | 72.6 | 0.2 | 512.3 | 183.7 | 186.6 | 0.2 |
| K | | 173.0 | 214.1 | 286.0 | 6.0 | 2414.3 | 133.6 | 767.0 | 30.4 |
| Ca | | 173.0 | 666.6 | 966.1 | 1.5 | 11950.2 | 144.9 | 1261.4 | 124.7 |
| Ti | | 173.0 | 16.8 | 13.5 | 1.1 | 89.9 | 80.5 | 42.9 | 2.1 |
| V | | 173.0 | 2.2 | 2.0 | 0.6 | 15.0 | 91.4 | 5.7 | 0.6 |
| Cr | | 173.0 | 0.7 | 0.8 | 0.5 | 8.0 | 115.3 | 2.0 | 0.5 |
| Mn | | 173.0 | 5.2 | 3.9 | 0.5 | 25.8 | 75.3 | 12.1 | 0.8 |
| Fe | | 173.0 | 191.3 | 158.2 | 0.9 | 1149.5 | 82.7 | 461.1 | 38.4 |
| Co | | 173.0 | 11.1 | 8.4 | 0.8 | 60.8 | 76.4 | 26.1 | 2.2 |
| Ni | | 173.0 | 2.3 | 0.8 | 2.1 | 10.8 | 34.8 | 2.3 | 2.1 |
| Cu | | 173.0 | 4.6 | 2.5 | 1.9 | 18.8 | 54.8 | 9.2 | 1.9 |
| Zn | | 173.0 | 19.7 | 22.7 | 2.2 | 149.8 | 115.1 | 66.2 | 2.2 |
| As | | 173.0 | 0.7 | 0.5 | 0.2 | 3.3 | 67.8 | 1.6 | 0.2 |
| Se | | 173.0 | 2.1 | 1.1 | 1.5 | 10.3 | 53.0 | 3.9 | 1.5 |
| Br | | 173.0 | 2.1 | 1.5 | 0.7 | 10.7 | 70.2 | 4.8 | 0.7 |
| Rb | | 173.0 | 1.8 | 1.4 | 0.6 | 8.7 | 80.1 | 4.6 | 0.6 |
| Sr | | 173.0 | 8.9 | 6.5 | 0.0 | 41.4 | 73.1 | 16.7 | 2.4 |
| Zr | | 173.0 | 3.6 | 2.3 | 0.0 | 18.5 | 65.8 | 6.9 | 0.4 |
| Mo | | 173.0 | 1.8 | 1.5 | 0.0 | 13.2 | 87.4 | 3.8 | 0.3 |
| Cd | | 173.0 | 0.8 | 1.1 | 0.1 | 9.3 | 132.3 | 2.9 | 0.1 |
| Ba | | 173.0 | 19.8 | 16.0 | 1.3 | 106.2 | 81.1 | 50.8 | 2.5 |
| Pb | | 173.0 | 8.9 | 6.2 | 3.7 | 43.3 | 69.9 | 19.4 | 3.7 |
| EC | | 173.0 | 13041.5 | 8723.8 | 226.0 | 38851.0 | 66.9 | 38851.0 | 3827.3 |
| $NH_4$ | | 173.0 | 659.8 | 525.2 | 9.1 | 2627.0 | 79.6 | 1825.3 | 108.7 |
| $SO_4$ | | 173.0 | 2688.9 | 1916.2 | 9.0 | 10326.6 | 71.3 | 6569.3 | 309.8 |
| $NO_3$ | | 173.0 | 1193.5 | 2003.6 | 9.0 | 10190.8 | 167.9 | 5971.4 | 9.1 |

## Table 6. Corelation matrix – Kumanovo dataset

| | PM2,5 | Na | Mg | Al | Si | P | S | Cl | K | Ca | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | As | Se | Br | Rb | Sr | Zr | Mo | Cd | Ba | Pb | EC | NH4 | SO4 | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PM2,5 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Na | 0.29 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Mg | 0.10 | 0.68 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Al | 0.06 | 0.45 | 0.92 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Si | 0.06 | 0.50 | 0.95 | 0.99 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| P | 0.04 | 0.62 | 0.88 | 0.81 | 0.85 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| S | 0.15 | 0.73 | 0.77 | 0.58 | 0.63 | 0.79 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cl | 0.61 | 0.76 | 0.25 | 0.08 | 0.10 | 0.25 | 0.40 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | |
| K | 0.70 | 0.66 | 0.29 | 0.18 | 0.19 | 0.26 | 0.42 | 0.89 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | |
| Ca | 0.14 | 0.67 | 0.83 | 0.60 | 0.69 | 0.70 | 0.71 | 0.28 | 0.30 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | |
| Ti | 0.18 | 0.54 | 0.92 | 0.96 | 0.97 | 0.82 | 0.61 | 0.22 | 0.29 | 0.68 | 1.00 | | | | | | | | | | | | | | | | | | | | | | |
| V | 0.20 | 0.59 | 0.93 | 0.91 | 0.93 | 0.82 | 0.68 | 0.23 | 0.29 | 0.74 | 0.95 | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| Cr | 0.11 | 0.70 | 0.88 | 0.73 | 0.78 | 0.75 | 0.70 | 0.27 | 0.24 | 0.82 | 0.76 | 0.83 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| Mn | 0.40 | 0.66 | 0.84 | 0.80 | 0.82 | 0.76 | 0.67 | 0.46 | 0.53 | 0.69 | 0.88 | 0.88 | 0.76 | 1.00 | | | | | | | | | | | | | | | | | | | |
| Fe | 0.25 | 0.63 | 0.93 | 0.91 | 0.93 | 0.83 | 0.67 | 0.32 | 0.36 | 0.73 | 0.95 | 0.94 | 0.84 | 0.93 | 1.00 | | | | | | | | | | | | | | | | | | |
| Co | 0.26 | 0.60 | 0.91 | 0.90 | 0.92 | 0.80 | 0.66 | 0.30 | 0.36 | 0.71 | 0.94 | 0.93 | 0.82 | 0.94 | 0.98 | 1.00 | | | | | | | | | | | | | | | | | |
| Ni | -0.01 | 0.51 | 0.62 | 0.36 | 0.46 | 0.47 | 0.56 | 0.11 | 0.12 | 0.82 | 0.40 | 0.53 | 0.70 | 0.44 | 0.46 | 0.45 | 1.00 | | | | | | | | | | | | | | | | |
| Cu | 0.43 | 0.36 | 0.27 | 0.21 | 0.19 | 0.27 | 0.30 | 0.41 | 0.44 | 0.21 | 0.28 | 0.37 | 0.33 | 0.46 | 0.37 | 0.40 | 0.17 | 1.00 | | | | | | | | | | | | | | | |
| Zn | 0.67 | 0.47 | 0.28 | 0.19 | 0.20 | 0.21 | 0.30 | 0.63 | 0.69 | 0.31 | 0.33 | 0.38 | 0.32 | 0.62 | 0.43 | 0.44 | 0.27 | 0.52 | 1.00 | | | | | | | | | | | | | | |
| As | 0.67 | 0.36 | 0.17 | 0.11 | 0.11 | 0.08 | 0.24 | 0.60 | 0.67 | 0.19 | 0.18 | 0.22 | 0.19 | 0.43 | 0.24 | 0.29 | 0.17 | 0.40 | 0.64 | 1.00 | | | | | | | | | | | | | |
| Se | 0.08 | -0.10 | -0.13 | -0.12 | -0.13 | -0.19 | -0.12 | -0.01 | 0.01 | -0.08 | -0.12 | -0.08 | -0.04 | -0.02 | -0.12 | -0.04 | 0.06 | 0.15 | 0.11 | 0.33 | 1.00 | | | | | | | | | | | | |
| Br | 0.67 | 0.35 | 0.15 | 0.08 | 0.09 | 0.07 | 0.22 | 0.59 | 0.67 | 0.18 | 0.16 | 0.20 | 0.17 | 0.41 | 0.22 | 0.27 | 0.17 | 0.41 | 0.63 | 0.98 | 0.37 | 1.00 | | | | | | | | | | | |
| Rb | 0.67 | 0.26 | 0.10 | 0.05 | 0.04 | -0.03 | 0.13 | 0.51 | 0.63 | 0.12 | 0.11 | 0.15 | 0.10 | 0.37 | 0.16 | 0.26 | 0.10 | 0.43 | 0.60 | 0.74 | 0.44 | 0.77 | 1.00 | | | | | | | | | | |
| Sr | 0.26 | 0.14 | 0.22 | 0.23 | 0.21 | 0.09 | 0.18 | 0.14 | 0.25 | 0.15 | 0.22 | 0.28 | 0.22 | 0.34 | 0.22 | 0.37 | 0.17 | 0.42 | 0.28 | 0.45 | 0.61 | 0.49 | 0.72 | 1.00 | | | | | | | | | |
| Zr | 0.07 | 0.66 | 0.86 | 0.76 | 0.79 | 0.99 | 0.87 | 0.30 | 0.31 | 0.70 | 0.77 | 0.78 | 0.74 | 0.76 | 0.80 | 0.78 | 0.48 | 0.30 | 0.23 | 0.12 | -0.17 | 0.11 | 0.01 | 0.12 | 1.00 | | | | | | | | |
| Mo | 0.15 | 0.73 | 0.77 | 0.58 | 0.63 | 0.79 | 1.00 | 0.40 | 0.42 | 0.71 | 0.61 | 0.68 | 0.70 | 0.67 | 0.67 | 0.66 | 0.56 | 0.31 | 0.30 | 0.24 | -0.12 | 0.22 | 0.13 | 0.18 | 0.86 | 1.00 | | | | | | | |
| Cd | 0.71 | 0.66 | 0.32 | 0.20 | 0.21 | 0.27 | 0.44 | 0.87 | 1.00 | 0.32 | 0.31 | 0.32 | 0.27 | 0.56 | 0.38 | 0.39 | 0.15 | 0.46 | 0.70 | 0.68 | 0.04 | 0.68 | 0.67 | 0.31 | 0.32 | 0.44 | 1.00 | | | | | | |
| Ba | 0.18 | 0.54 | 0.92 | 0.96 | 0.97 | 0.81 | 0.60 | 0.22 | 0.29 | 0.67 | 1.00 | 0.95 | 0.75 | 0.87 | 0.95 | 0.94 | 0.40 | 0.28 | 0.32 | 0.18 | -0.12 | 0.16 | 0.11 | 0.22 | 0.76 | 0.60 | 0.30 | 1.00 | | | | | |
| Pb | 0.63 | 0.26 | 0.11 | 0.07 | 0.07 | 0.03 | 0.17 | 0.48 | 0.55 | 0.14 | 0.16 | 0.21 | 0.15 | 0.42 | 0.21 | 0.30 | 0.10 | 0.48 | 0.64 | 0.70 | 0.37 | 0.71 | 0.79 | 0.61 | 0.07 | 0.17 | 0.58 | 0.16 | 1.00 | | | | |
| EC | 0.68 | 0.04 | -0.02 | -0.03 | -0.02 | -0.14 | -0.03 | 0.28 | 0.39 | 0.07 | 0.04 | 0.08 | -0.01 | 0.18 | 0.09 | 0.11 | 0.02 | 0.22 | 0.46 | 0.54 | 0.14 | 0.56 | 0.57 | 0.29 | -0.13 | -0.03 | 0.41 | 0.04 | 0.51 | 1.00 | | | |
| NH4 | 0.53 | 0.15 | 0.06 | 0.03 | 0.02 | 0.09 | 0.37 | 0.35 | 0.40 | 0.01 | 0.08 | 0.13 | 0.07 | 0.26 | 0.14 | 0.20 | -0.02 | 0.40 | 0.43 | 0.53 | 0.25 | 0.54 | 0.51 | 0.43 | 0.18 | 0.37 | 0.42 | 0.08 | 0.55 | 0.37 | 1.00 | | |
| SO4 | 0.69 | 0.34 | 0.22 | 0.20 | 0.18 | 0.19 | 0.41 | 0.53 | 0.62 | 0.15 | 0.28 | 0.29 | 0.15 | 0.45 | 0.31 | 0.34 | 0.01 | 0.43 | 0.55 | 0.64 | 0.11 | 0.64 | 0.59 | 0.35 | 0.25 | 0.41 | 0.64 | 0.28 | 0.56 | 0.48 | 0.75 | 1.00 | |
| NO3 | 0.80 | 0.33 | 0.02 | -0.08 | -0.07 | -0.08 | 0.14 | 0.65 | 0.69 | 0.13 | 0.05 | 0.11 | 0.11 | 0.31 | 0.16 | 0.18 | 0.07 | 0.50 | 0.70 | 0.73 | 0.20 | 0.74 | 0.69 | 0.34 | -0.03 | 0.14 | 0.70 | 0.05 | 0.66 | 0.61 | 0.67 | 0.68 | 1.00 |

## Temporal variations

Temporal variations of PM2.5 concentrations help clarify the sources and contributing factors that lead to air pollution [15, 16]. Diurnal and seasonal trends can distinguish between traffic-related, industrial, and meteorological impacts on PM2.5 concentrations. A detailed understanding of PM2.5 temporal patterns can inform the development of effective strategies for managing air quality and policies [17]. This includes implementing targeted emission control measures, optimizing monitoring networks, and issuing timely public advisories. Since the temporal variations in PM2.5 are influenced by meteorological factors such as temperature, humidity, and wind patterns [18], comprehending these relationships is essential for assessing the potential impacts of climate change on air quality.

Temporal variations are assessed using gravimetric data in conjunction with real-time data from collocated referent monitoring stations.

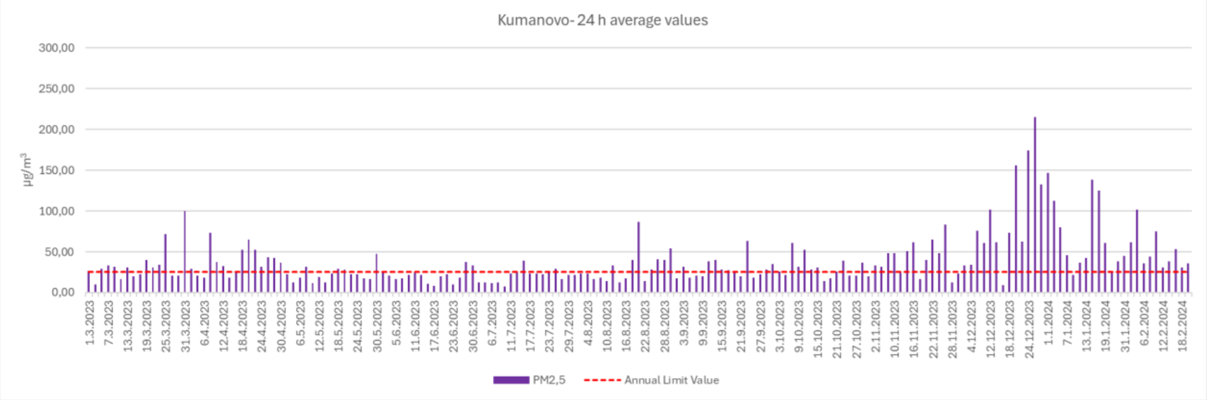


Figure 30. PM 2.5 – daily average concentrations from March 2023 to March 2024

The daily average PM2.5 concentrations measured at the Kumanovo monitoring site show significant daily and seasonal variations, exceeding all national and European Union limits, targets, and thresholds for protecting human health. Daily readings displayed considerable variability, with a standard deviation of 31.7 μg/m$^3$ and a coefficient of variation of 82.4 %.

The concentrations ranged from a minimum of 7.4 μg/m$^3$ to a maximum of 215 μg/m$^3$, resulting in an average annual value of 38.5 μg/m$^3$, which exceeds the annual threshold limit value of 25 μg/m$^3$ by approximately 54 %. The percentage of days that surpass the annual limit for PM2.5 (25 μg/m$^3$) was concerning at 57.2 % (99 out of 173 valid daily readings), with much higher levels seen in the colder months (51.7 μg/m$^3$) compared to still high levels in the warmer months (26.7 μg/m$^3$).

## PM 2.5 chemical composition

The chemical compositions of PM2.5 differ across Europe and on average, Central Europe has more carbonaceous matter in PM2.5, North-western Europe has more nitrate, and southern Europe has more mineral dust in all fractions [20].

The contribution of mineral (soil) particles measured in Kumanovo is similar to the values recorded in Skopje and is within the range identified in certain regions of Southern Europe, achieving an annual average of around 3 % [20, 21]. Elements like Mg, Al, Si, Ca, Ti and Fe, usually used as tracers for soil dust, are well corelated, indicating common source for these elements and providing clear identification of this source in subsequent factor analysis.

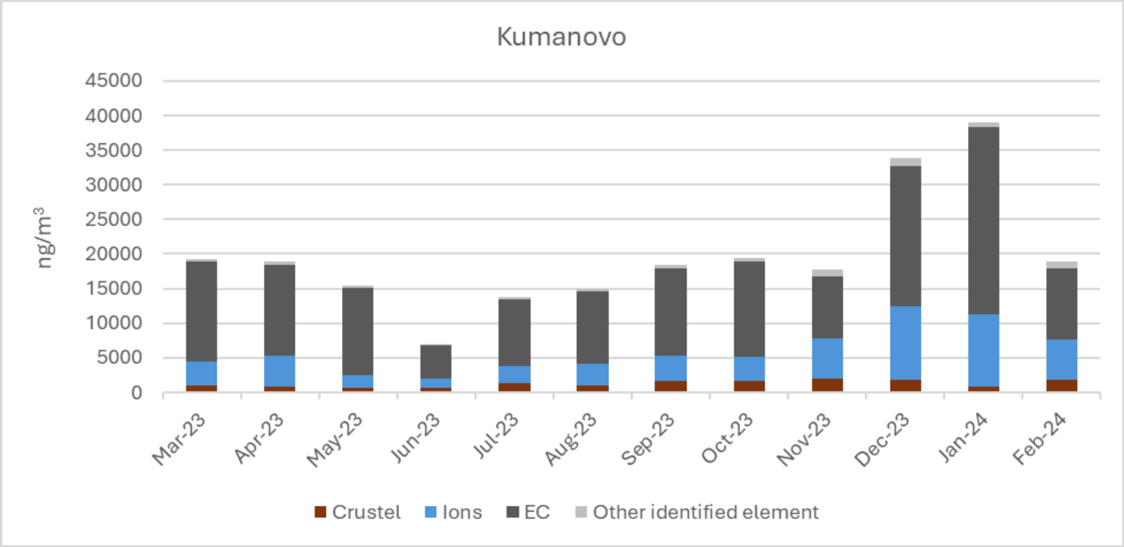
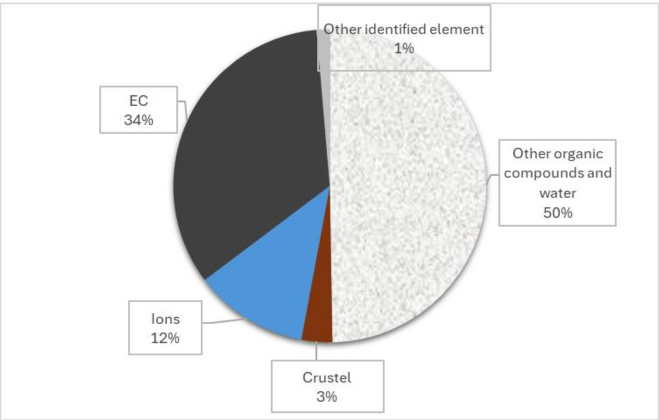


**Figure 31. Major components and elemental groups identified**

Sea salt contributions are negligible, as would be expected for a typically continental location. The contributions of ions (sulphates and nitrates) are markedly lower than those documented throughout Europe, with a combined contribution of 12 % falling within the range of values observed in Skopje [20, 21]. This may be attributed to several factors; however, it is important to note the relatively low average concentrations of gaseous precursors such as sulfuric and nitrous oxides.

Elemental carbon (EC) contributions in the urban area of Kumanovo exceed European averages, with an average of 34 %. This figure is also significantly higher than that observed in Skopje. This discrepancy likely reflects the local sources of emissions, with wood combustion identified as the most significant single source of particulate matter. Traffic emissions, particularly exhaust from service and older diesel-powered vehicles, can also impact this situation.



| | Crustal | EC | Ions |
|---|---|---|---|
| N-W Europe | 5 | 7 | 37 |
| Southern Europe | 11 | 8 | 22 |
| Central Europe | 5 | 14 | 32 |
| Skopje | 4 | 23 | 16 |
| Kumanovo | 3 | 34 | 12 |

**Figure 32. Contribution of major particulate matter components [20, 21]**

Assessment of regulated metals, specifically lead, arsenic, cadmium, and nickel, was conducted only for those metals that successfully underwent external quality assessment procedures, which included only lead and nickel. The results for arsenic and cadmium are available; however, they are excluded from direct comparison due to the significant uncertainty associated with them.

It was determined that the average annual concentrations of lead and nickel found were within the annual limit threshold values as specified in Directives 2008/51/EC and 2004/71/EC.

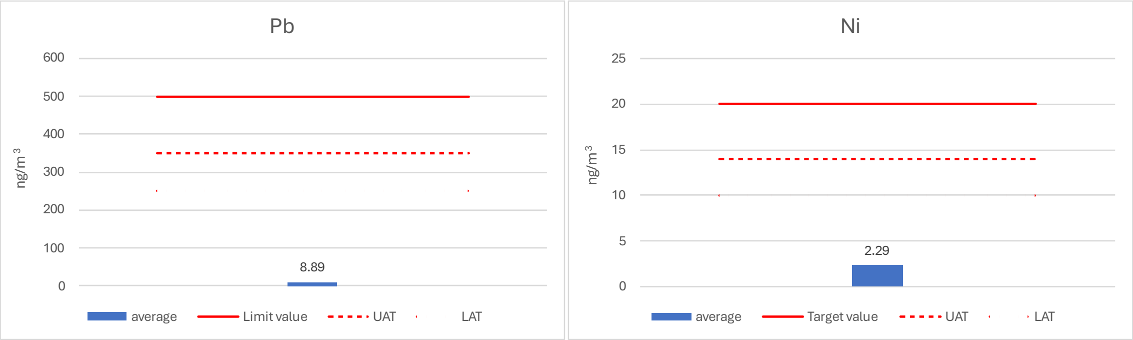


**Figure 33. Average monthly concentrations of lead (Pb) and nickel (Ni) in Kumanovo**

## 5. Positive Matrix Factorisation

Environmental monitoring data are increasingly being handled in terms of mathematical models, which allow for the management of a variety of datasets with multiple observations to be performed. Different modeling techniques are available depending on the type of known information (input data) and the sort of results that would be obtained (output data) that are desired.

Source apportionment (SA) is the practice of obtaining information about pollution sources and the amount of pollution that each source contributes to the level of ambient air pollution. Emission inventories, source-oriented models, and receptor-oriented models are three methods that can be employed to accomplish this task.

In recent years, receptor-oriented models (also known as receptor models (RMs)) have gained prominence in environmental sciences. These models are utilized to extract information from datasets containing various features (chemical or physical properties) associated with the measured samples. For instance, they can assess the contribution of contamination and pollutant sources across different sample types, beginning with the data provided by the samples (recorded at the monitoring site) and advancing to the point of effect, or receptor.

Receptor models are also referred to as multivariate methods because they analyze datasets that consist of numerous numerical values as a whole. More specifically, receptor models are mathematical methodologies designed to quantify the contribution of sources to samples based on their composition or fingerprints. To differentiate impacts, the composition or speciation is identified using media-specific analytical methods, and the identification of key species or combinations of species is necessary. A speciated data set can be considered of as a data matrix X with i by j dimensions, in which i samples and j chemical species were measured with u uncertainty.

The goal of receptor models is to solve the chemical mass balance (CMB) in Equation 1, between measured species concentrations and source profiles, where p is the number of factors, f is each source's element profile, g is each factor's mass in each sample, and $e_{ij}$ is the "remaining" for each element/sample.

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

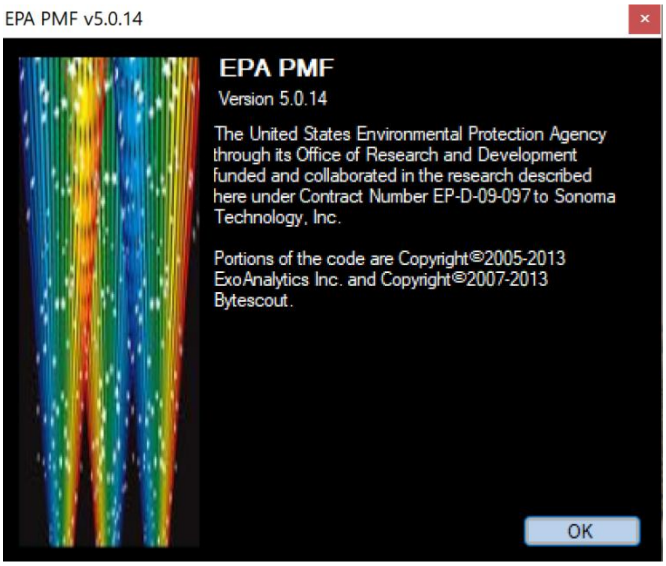
A dataset containing a vast amount of data consisting of chemical elements (such as elemental concentrations) acquired from a large number of observations (samples) is required to find the answer. The larger the data matrix, the more likely the model is to uncover separate factors that can be used as sources. The number of samples required can vary depending on prior knowledge of the sources and the RMs methodology chosen (e.g., CMB vs. PMF).

If the number and nature (composition profiles/fingerprints) of the sources in the study area are known, then the only unknown term of equation (1) is the mass contribution of each source to each sample. To solve the chemical mass balance and to elicit information on sources type, number and contribution starting from observations (i.e. element concentrations data set) at receptor site, different factor analysis methods (multivariate methods) have been developed. Common factor analysis methods used include Principal Component Analysis (PCA), Unmix, Target Transformation Factor Analysis (TTFA), Positive Matrix Factorization (PMF) and Multilinear Engine (ME).

Dr. Pentti Paatero (Department of Physics, University of Helsinki) created Positive Matrix Factorization (PMF) in the mid-1990s to establish a new method for the analysis of multivariate data that addressed several drawbacks of the PCA.

PMF uses error estimates to weight data values and imposes non-negativity constraints in the factor computational process. The algorithm accomplishes weighted least squares fit with the objective of minimizing Q, a function of the residuals weighted by the uncertainties of the species concentrations in the data matrix. The PMF factor model can be written as $X = G \cdot F + E$, where X is the known $n \cdot m$ matrix of the m measured chemical species in n samples. G is an $n \cdot p$ matrix of factor (source) contribution in every sample (time series). F is a $p \cdot m$ matrix of factor compositions (factor profiles). G and F are factor matrices to be determined and E is defined as a residual matrix, i.e. the difference between the measured X and the modeled $Y = G \cdot F$.

In this study, the free software US-EPA PMF 5.0 version 5.0.14 [22], implementing the ME-2 algorithm developed by Paatero (1999), was used.



**EPA PMF**

Version 5.0.14

The United States Environmental Protection Agency through its Office of Research and Development funded and collaborated in the research described here under Contract Number EP-D-09-097 to Sonoma Technology, Inc.

Portions of the code are Copyright©2005-2013 ExoAnalytics Inc. and Copyright©2007-2013 Bytescout.

**Figure 34. Free software US-EPA PMF 5.0 version 5.0.14 – splash screen**

PMF was first employed in studies of air pollution and source apportionment [23, 24] as well as precipitation investigations [25]. Air quality and source apportionment applications [26, 27] have gain rapid popularity in recent years, but PMF has also been used on lake sediments [28], wastewater [29, 30], and soils [31]. This multivariate factor analysis tool has been used to analyze a variety of data, including 24-hour speciated PM2.5, size-resolved aerosol, deposition, air toxics, high time resolution measurements from aerosol mass spectrometers (AMS), and volatile organic compound (VOC) data.

The use of known experimental uncertainties as input data allows for individual handling of matrix members and can handle missing or below-detection-limit data, which is a prevalent feature of environmental monitoring. Because the PMF results are quantitative, it is feasible to determine the composition of the sources determined by the model.

Equation 2 was used to determine the uncertainty of the utilized method for each element separately, and Equation 3 was used to determine the uncertainty of the instrument for each element separately:

$$u = \sqrt{{U_{instrument}}^2 + {U_{CRM}}^2 + {U_{sampling}}^2} \quad (\%) \qquad (2)$$

$$U_{instrument} = \frac{STDEV}{average} * 100 \quad (\%) \qquad (3)$$

Where $U_{instrument}$ - uncertainty of the used instrument, $U_{CRM}$ - uncertainty of the used certified referent material, $U_{sampling}$ - uncertainty of the sampling.

Before data processing, various basic statistical tests—such as dispersion, distribution, correlation matrices, linear regression, and time trends—were conducted to examine the relationships among the variables.

## 5.1. Input data and PMF model setting

Species lists included water-soluble ions $NH_4^+$, $SO_4^{2-}$, $NO_3^-$, elemental carbon (EC), and following elements; Na, Mg Al, Si, Ca, K, Ti, Fe, P, S, Cl, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Ba and Pb.

Following the EU protocol for receptor models [32], the data were initially processed to remove values that could potentially degrade the quality of the analysis. To validate the data and identify atypical values when compared to the rest of the dataset, scatter plots and time series analysis were employed. After data validation, the original datasets included 32 species and 173 daily samples.

As recommended in EU protocol for receptor models [32], data below the limit of detection (LOD) were substituted by half of the LOD and the uncertainties were set to 5/6 of the LOD. Missing data were substituted by the geometric mean of the measured concentrations and the corresponding uncertainties were set as 4 times this geometric mean [33].

Species with high noise were down-weighted based on their signal-to-noise (S/N) ratio to reduce the influence of poor variables on the PMF analysis. Species with S/N lower than 0.5 were considered as bad variables and excluded from the analysis, and species with S/N between 0.5 and 1 were defined as weak variables and down-weighted by increasing the uncertainty as recommended in the PMF users guideline. Using this approach Ni, As and Cd were set as a weak variables. The EC also was set as a weak although S/N was above 8. PM 2.5 was also set as total (week) variable in order to reduce influence on profiles contribution.

Additional information regarding the modelling approach is provided in Source Apportionment Study for Skopje urban area –identification of main sources of ambient air pollution [34].

## 5.2. Factor attribution to sources

Final PMF solution for Kumanovo datasets included 6 factors. Factors were attributed to their sources though a quantitative and qualitative comparisons of the factor chemical profile with PM profiles reported EC-JRC SPECIEUROPE data base and profiles from previous source apportionment studies available in the literature.

In addition, the standardised identity distance (SID) and the Pearson coefficient, expressed as Pearson distance (PD = 1 - r), were used to calculate the similarity between the factors and the reference source profiles available in the public datasets: EC-JRC SPECIEUROPE and US-EPA SPECIATE [35]. The Delta SA tool [10] was used to complete the work.

Factors that were identified in municipality of Kumanovo are as follows: biomass burning, traffic, fuel and residual oil, road and soil dust, open fire and waste burning and secondary aerosols.

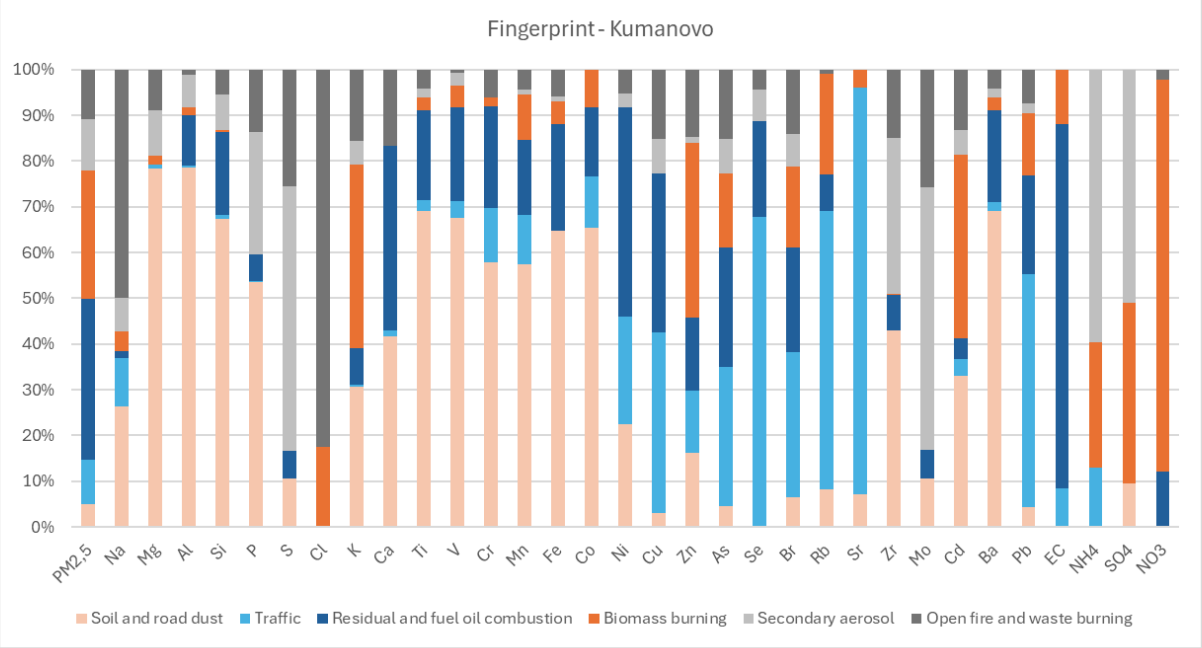


**Figure 35. Factor fingerprint for Kumanovo**

Biomass burning incorporates emissions from various types of wood-burning stoves and boilers primarily used for residential heating. Key species associated with this factor include EC, K, Cl, $NO_3^-$, and Rb. K is produced from the combustion of wood lignin [36, 37]. Although this element can also be emitted from other sources, such as soil dust [38], K has been extensively used as an inorganic tracer to apportion biomass burning contributions to ambient aerosol. It has been associated with biomass burning in PMF source profiles in Tirana, Skopje, Athens, Belgrade, Banja Luka, Debrecen, Chisnay, Zagreb, and Krakow [39].

Both biomass burning and coal combustion can release Cl, especially in the colder months [40]. The PMF source profiles in Belgrade and Banja Luka also link it to biomass burning [39].

In addition, $NO_3^-$ and $NH_4^+$ have significantly contributed to the biomass burning factor. Biomass burning serves as an important source of $NH_3$ [41], which quickly reacts with $HNO_3$ to form $NH_4NO_3$ aerosols. The occurrence of $NH_4NO_3$ aerosols in biomass burning plumes has also been documented previously [41, 42].

Evaluation of seasonal patterns of this factor clearly confirms attribution of this factor to biomass burning emissions, that usually occur only during the cold months.

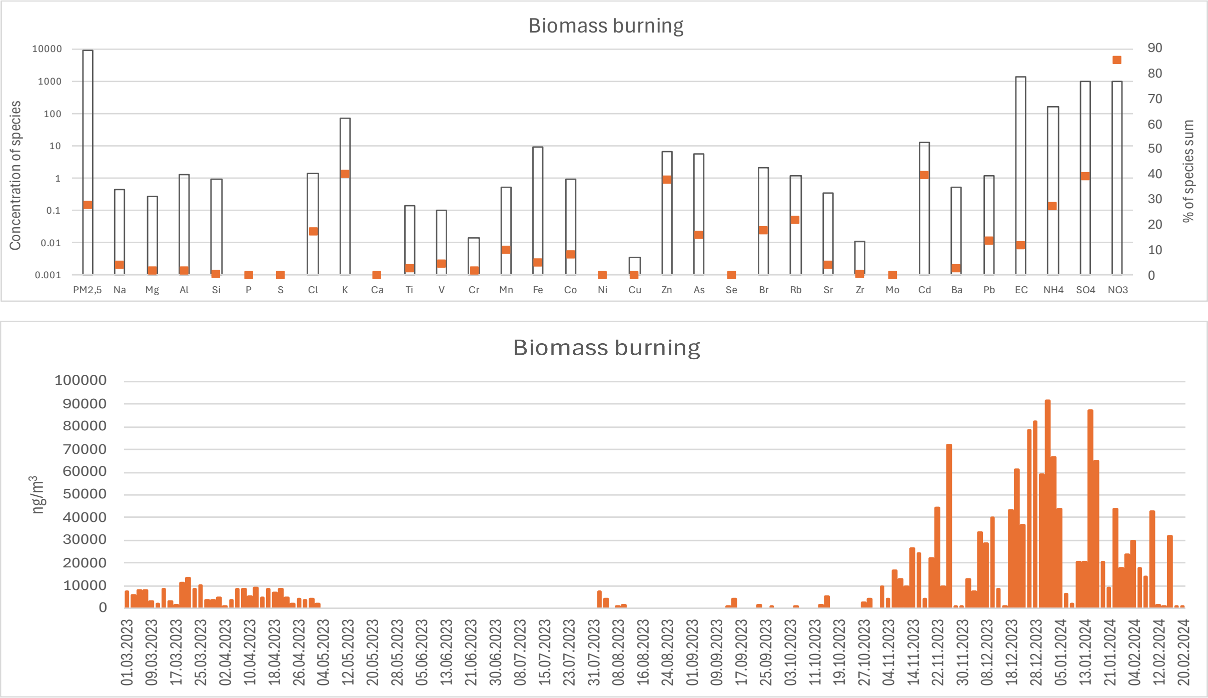


**Figure 36. Biomass burning factor profiles in Kumanovo**

Traffic includes particles from several different sources, including vehicle exhaust, mechanical abrasions of brakes and tires, resuspended road dust, and road salting. Each source has its own specific fingerprints and can be identified by elements such as EC, Ba, Cu, Mn, Pb, and Zn, as well as crustal species like Mg, Al, Si, Ca, Fe, and Ti, or Na and Cl in the case of winter road salting.

Vehicle exhaust, which includes both diesel and gasoline emissions, is composed of a high percentage of organic and elemental carbon, along with Fe, Pb, Zn, Al, Cu, and sulphate. Similar species have also been associated with traffic in PMF source profiles across many urban areas in Europe and Central Asia [39].

Zn is a major additive in lubricant oil. Zn and Fe can also originate from tire abrasion, brake linings, lubricants, corrosion of vehicular parts, and tailpipe emissions [43-46].

Since the use of Pb additives in gasoline has been banned, the observed Pb emissions are likely associated with wear (from tires or brakes) rather than fuel combustion [47].

Fe and Al are likely connected to vehicle part wear, such as from tire and brake wear, as well as road abrasion, and these elements are common in sampling sites located near major roads.

These results indicate the contribution of both exhaust and non-exhaust traffic emissions to various factors associated with traffic. The elemental composition of particulate emissions linked to traffic can vary significantly due to differences in traffic volume and patterns, vehicle fleet characteristics, climate, and the geology of the region [48]; however, similar elements (Cu, Mn, Zn, Pb, Fe, and EC) have been identified as key species in PMF source profiles across most urban areas in Europe and Central Asia [39].

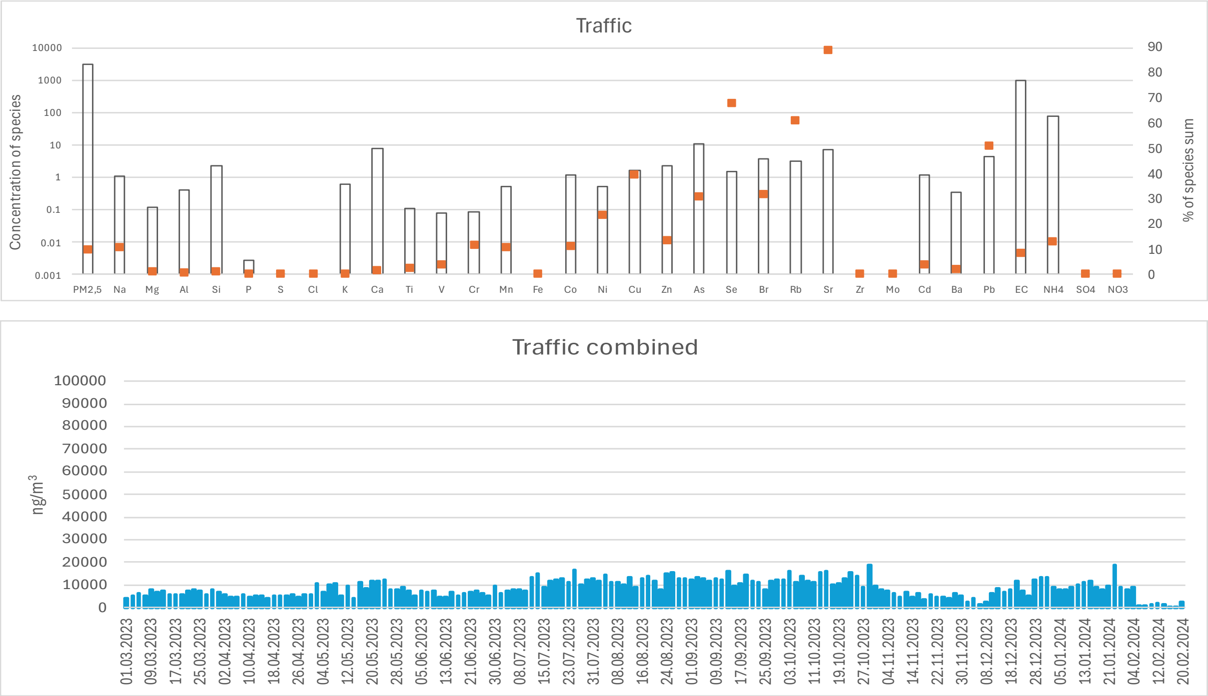


**Figure 37. Traffic associated factors for Kumanovo dataset**

Fuel and residual oil combustion is a stand-alone factor that includes emissions from a wide range of sources, the majority of which are larger buildings heating systems (schools, hospitals, and other public institutions), industrial combustion emissions and to some extent older diesel-powered vehicles emissions, principally composed of EC, V, Cd and Ni [41, 42].

Organic carbon, sodium, and water-soluble ions including nitrates and sulphates are common key species for fuel oil emissions. The presence of V and Ni is also common marker. Water-soluble ions, V, Fe, and Ni are also important species for residual oil combustion, but increased quantities of elemental carbon, rather than organic carbon, are common for this source.

Vanadium, either alone or in conjunction with nickel, is a prevalent marker in PMF source profiles, in most European and Central Asian urban areas [39].

Soil or mineral dust usually originates from construction/demolition activities, dust resuspension and wind erosion processes. This source is commonly identified with so called crustal elements like Mg, Al, Si, Ca, Fe and Ti [49]. Silicon and Ca are usually most abundant elements, followed by Fe, Al, Mg, and Ti with variations due to local geology.

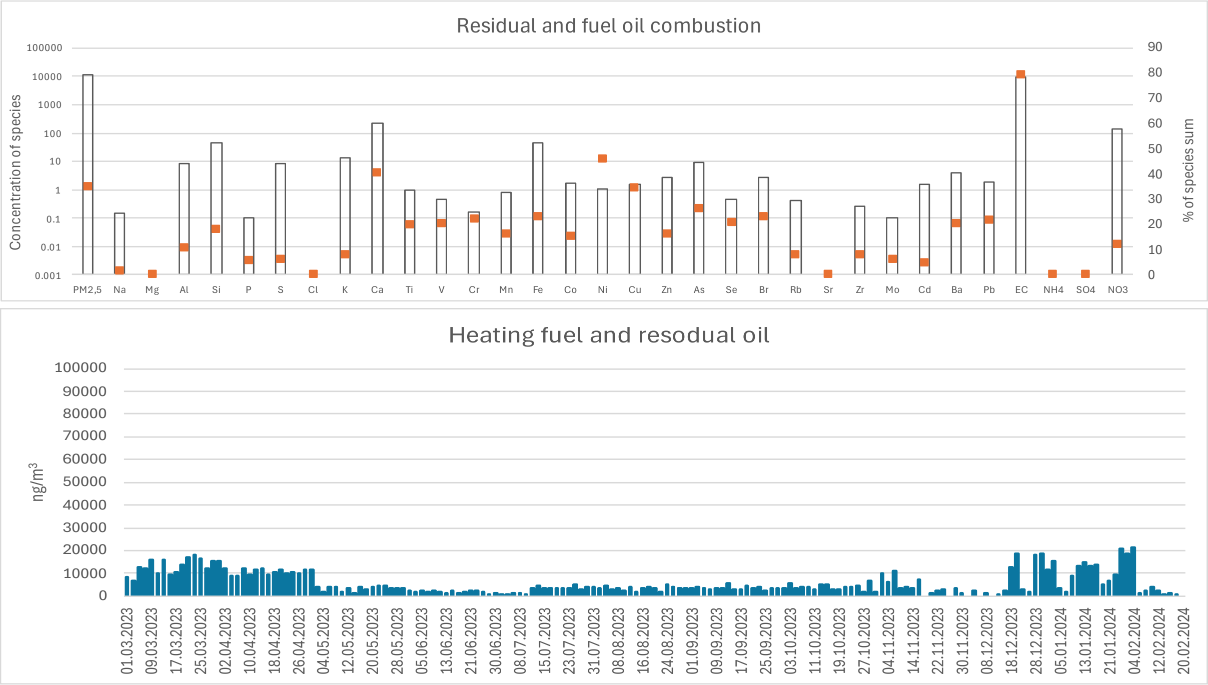


**Figure 38. Fuel and residual oil factor profiles**

Other research studies also reported significant contribution of soil dust to PM2.5 mass, suggesting that soil dust is an important contributor to PM2.5 mass especially in summertime [50, 51]. Similar elements (Ca, Fe, Al, Si, Ba, Na and Ti) were identified as key species in PMF source profiles in most European and Central Asia urban areas [39]. Silicon and calcium are also prevalent species in the construction related source's chemical profile. Chemical profile of construction source also includes Si, Ca, Al and Fe, but also OC, EC and sulphates have significant contribution.

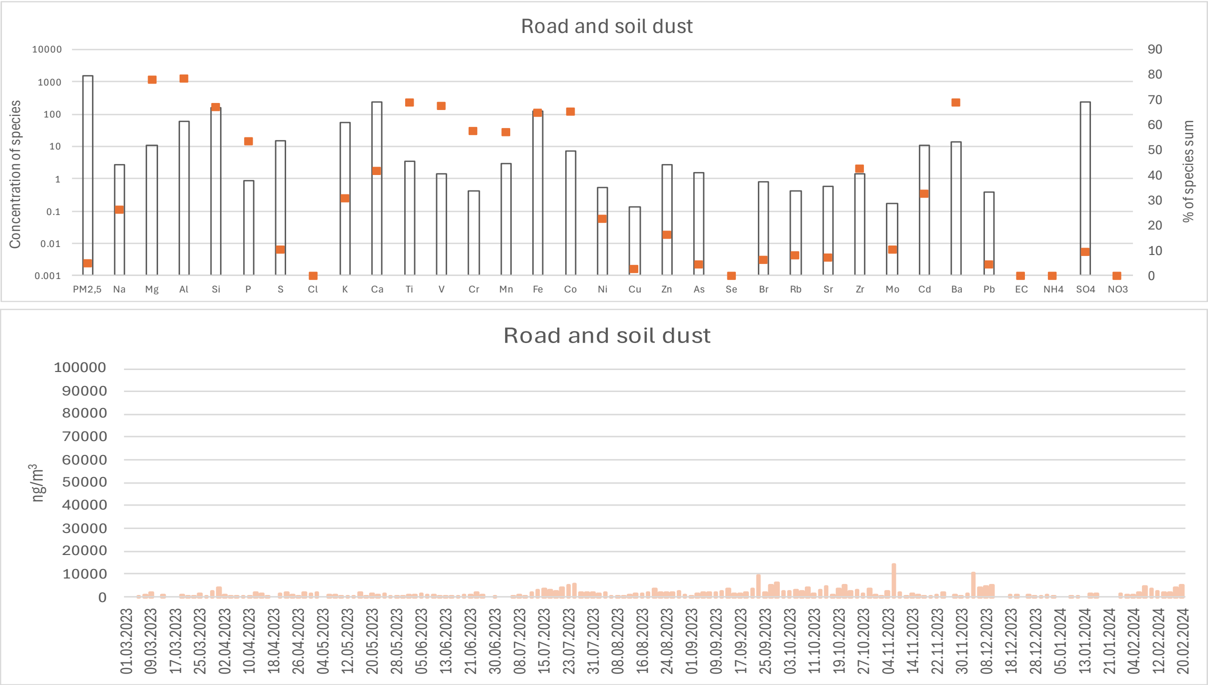


**Figure 39. Mineral dust factor profiles**

All types of low efficiency burning of agricultural and garden waste, as well as other types of waste, are classified as open fire burning. This factor is identified by high contribution Cl, As, Cd and Rb, but also includes some specific metals like Pb, Cu and Ni. Elemental carbon, Br, Co, V, Ti, and As were also found as important species in an analysis of agricultural waste open burning profiles, conducted in the Thessaloniki area in Northern Greece (SPECIEUROPE data base). According to Lemieux [52] depending on the source, varying amounts of metals such as lead (Pb) or mercury (Hg) may be emitted. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) or polychlorinated biphenyls (PCBs) can be emitted as well.

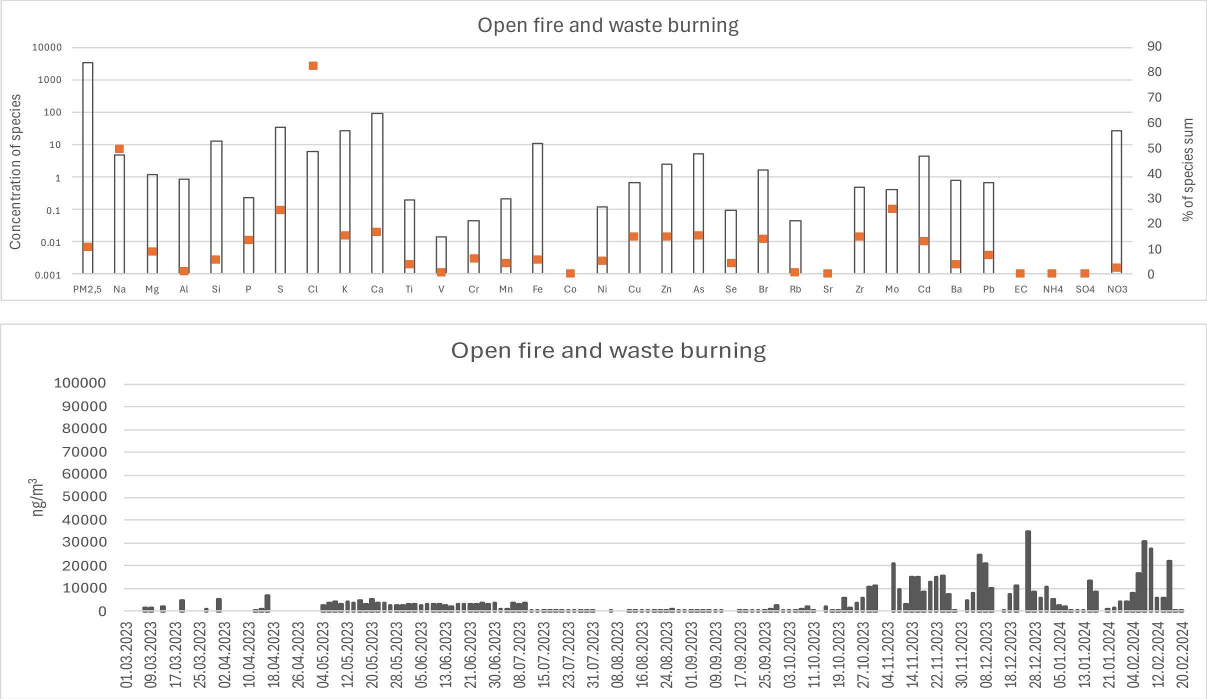


**Figure 40. Open fire burning factor profile**

Secondary aerosols contribute the most during the coldest and warmest months, when there are high levels of gaseous percussors in the winter and high temperatures in the summer.

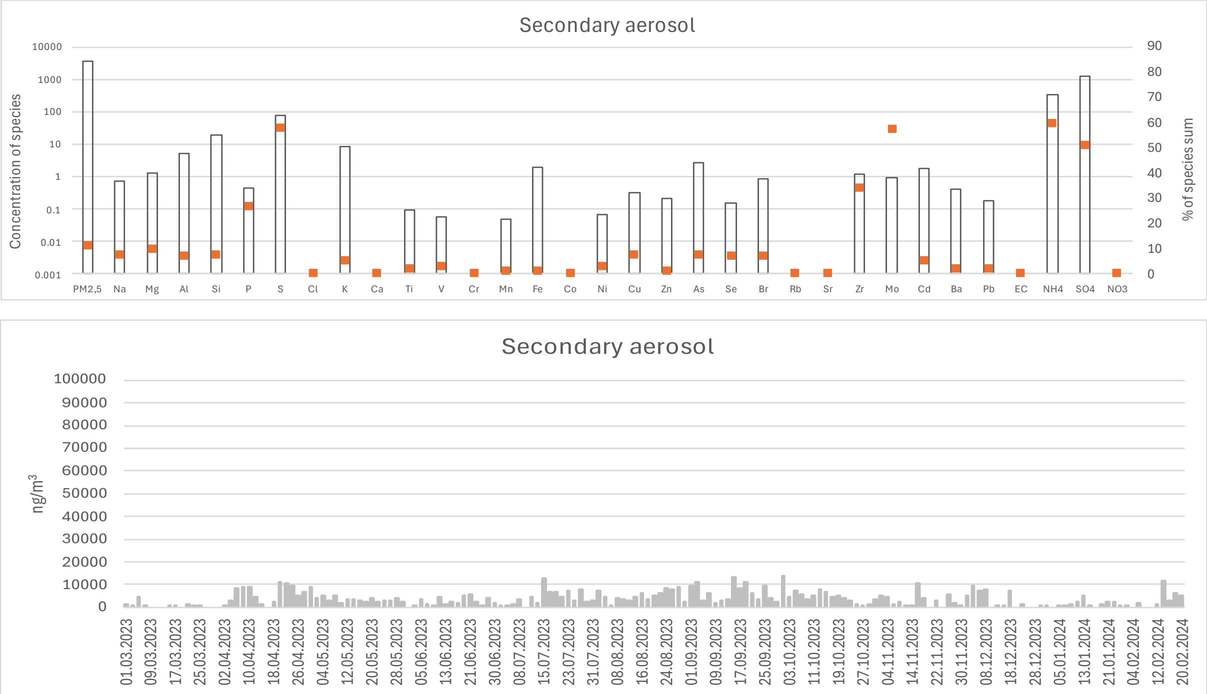


**Figure 41. Secondary Aerosols factor profile**

## 5.3. Sources Contribution

The contribution of each source to the total particle mass (PM 2.5) was determined using data from measurements and modelling exercises. The primary sources identified for Kumanovo include biomass burning, open fires and waste burning, traffic, secondary aerosols, road and soil dust, and fuel and residual oil combustion. The traffic contribution was determined by combining modelled values from two identified sources: traffic and the combustion of fuel and residual oil. Because of the resemblance in exhaust emissions from older diesel vehicles and fuel oil-burning boilers, a significant amount, 70 %, of fuel oil contributions during warmer periods are attributed to traffic sources.

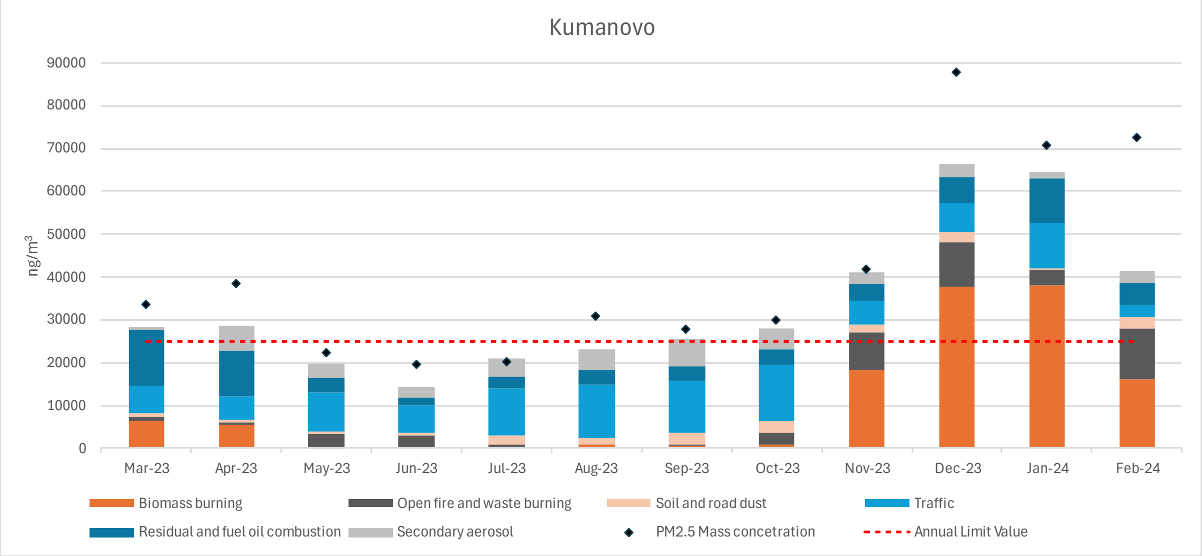


**Figure 42. Average monthly contributions to total particulate mass (PM 2.5) – Kumanovo**

Biomass burning was a significant source in the municipality of Kumanovo during the winter months, with the biggest contribution to total particle mass occurring in November, December, January, February, and March, while having minimal impact during the summer months. Biomass burning mostly belongs to residential heating; however, it also includes biomass burning in bakeries, restaurants, and small industrial establishments that utilize wood for heating or generating thermal energy for their operational processes. The average monthly contribution of biomass burning over the winter was up to 37.9 µg/m$^3$, and during the winter season, this source alone exceeds the yearly limit value for PM 2.5, set at 25 µg/m$^3$. The relative contributions (%) of biomass burning to total particle mass demonstrate significant seasonal variability, with this source accounting to 58.8 % during winter months, and although entirely seasonal, biomass burning accounts for a significant annual relative contribution of 31 %.

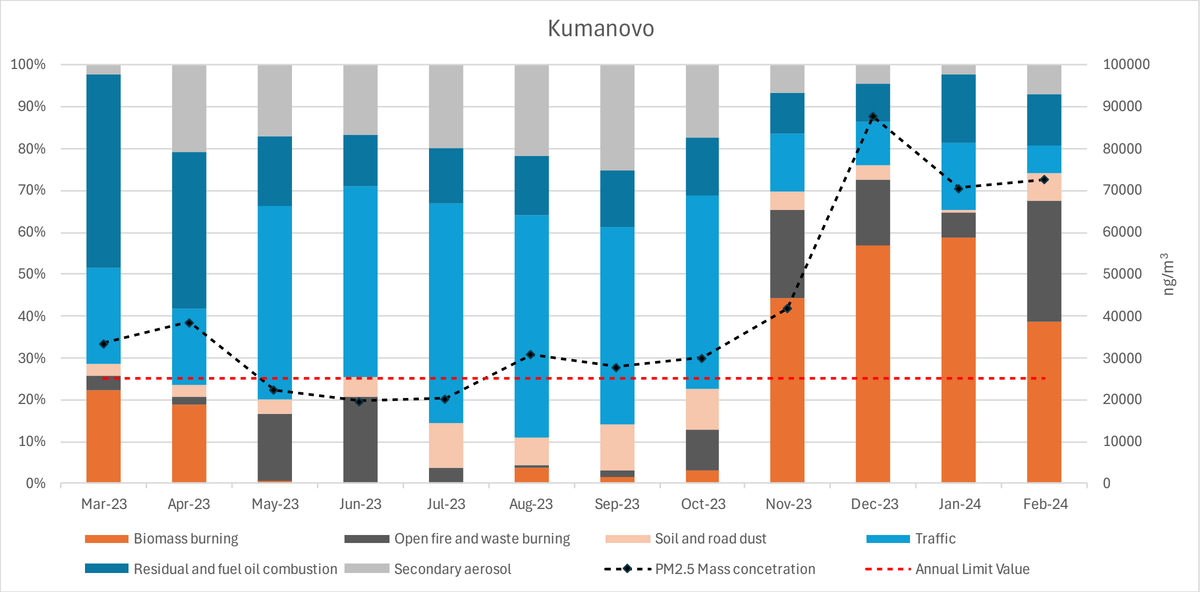


**Figure 43. Relative monthly contribution – Kumanovo**

Annually, traffic represents the second largest air pollution source, demonstrating a steady contribution throughout the year, with a notable increase during the summer and fall months, ranging from 2.7 to 13.0 µg/m$^3$. The annual relative contribution of traffic constituted 25 % of the total particulate mass (PM 2.5), with monthly relative contributions varying between 6.6% and 53.1 %. This source includes emissions resulting from vehicles exhaust, brake and tire wear, in addition to the combustion of oil in older diesel engines, such as those found in tractors, trucks, and older passenger vehicles lacking exhaust control devices.

Road and soil dust, additionally referred to as mineral dust, comprises particulate matter primarily originating from construction activities and the resuspension of deposits on roadways. This source significantly contributes to total particulate mass (PM2.5), with an increasing contribution during dry seasons, ranging from 0.4 to 2.8 µg/m$^3$. The monthly contributions from this source vary between 0.6 and 11.1 %, but the annual relative contribution attains 5 %.

Combustion of fuel and residual oil mainly comes from furnaces for heating public facilities and buildings (kindergartens, schools, hospitals), as well as in industrial facilities for heat production or some other technological processes. Fuel and residual oil contribute from 1.7 and 13.1 µg/m$^3$ to total particulate mass. This source occurs consistent over the year. Annual relative contribution of fuel and residual oil combustion accounted for 17 % of the total particulate mass (PM 2.5) mass. Relative monthly contribution ranged from 9.1 to 37.3 %.

Open fires and waste burning include the combustion of crop residue, agricultural and garden waste materials, as well as landfill fires and wildfires. This factor also includes the combustion of diverse waste materials in household stoves or small industrial boilers and is predominantly observable during the spring and early summer months, with an increased contribution in the autumn and winter periods and the relative monthly contribution of this source reaches up to 12 µg/m$^3$. The monthly contribution from this source reaches up to 28.9 %, while the annual contribution is 11 %.

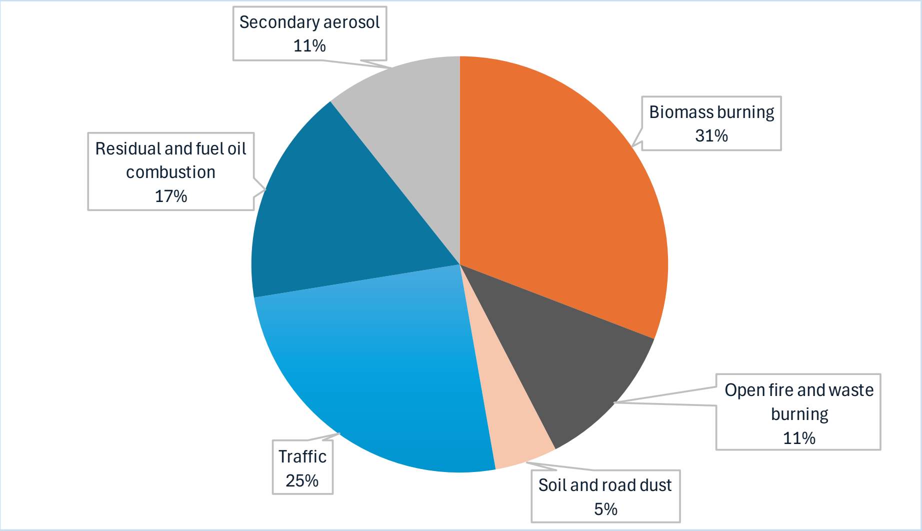


**Figure 44. Relative annual contribution of PM 2.5 sources at Kumanovo**

Secondary aerosols are particles that are not directly emitted but are generated by various chemical reactions in the atmosphere, influenced by sunlight, ozone, and humidity, ultimately resulting in the formation of "secondary aerosols." Secondary aerosols demonstrate their greatest contribution during the coldest and warmest months, perhaps linked to elevated quantities of gaseous precursors in winter and photochemical reactions resulting from high temperatures in summer. The annual relative contribution of secondary aerosols was 11 % of the total particle mass (PM2.5), with monthly contributions displaying significant variability up to 25.3 %.

## 6. Conclusions and recommendations

The urban region of Kumanovo suffers poor air quality for an extended period of time. Particulate matter (PM 10) concentrations continuously exceed the set threshold limits. Between 2017 and 2021, Kumanovo's average annual PM10 concentrations and the number of 24-hour limit value exceedances are continuously greater than the recommended levels.

The AMBICON Laboratory carried out this Source Apportionment Study to obtain information on pollution sources and their contributions to ambient air pollution in Kumanovo. The activities followed the strict guidelines in the European handbook on air pollution source apportionment using receptor models (Revised edition 2019, JRC) and included a year-long program for collecting and analyzing air samples, which helped create a complex model to identify pollution sources. The sampling program started on March 1, 2023, and until the March 7, 2024, 173 samples were collected, with a 24-hour sample being taken every other day. The sampling process was executed in strict compliance with the standard gravimetric measurement method for determining the mass concentration of PM10/PM2.5 suspended particulate matter (EN 12341:2014). Energy dispersive X-ray fluorescence (ED-XRF) was used to analyze the elements, an optical transmissometer measured the amount of elemental carbon, and spectrophotometry helped identify water-soluble ions.

The daily average PM2.5 concentrations measured at the Kumanovo monitoring site exhibit significant daily and seasonal variations, exceeding all European Union limits, targets, and thresholds for human health protection. Concentrations measured ranged from a minimum of 7.4 μg/m$^3$ to a maximum of 215.0 μg/m$^3$, resulting in an average annual value of 38.5 μg/m$^3$, which exceeds the annual threshold limit value of 25 μg/m$^3$ by high 54%. During the heating season, the concentrations are significantly higher than in the warm months. The average value for the months of the heating season is 51.7 μg/m$^3$ and is more than 60% higher than the average in the warm months. In the spring and summer months, the average is 26.7 μg/m$^3$. However, the average concentration even for the warm months exceeds the annual limit value by about 6 %. The percentage of days surpassing the annual limit for PM 2.5 (25 μg/m$^3$) was an alarming 57.2 % (99 out of 173 valid daily readings).

Using the data from measurements and modelling exercise, contribution of each source to total particulate mass (PM 2.5) was calculated. The major sources identified for Kumanovo include biomass burning, open fire and waste burning, traffic, secondary aerosols, road and soil dust, and fuel and residual oil burning.

Biomass burning is also one of the most important sources with relative contribution to total particulate mass accounting up to 58.8 % during winter months, and although entirely seasonal, biomass burning accounts for a significant annual relative contribution of 31%. On annual level, traffic is the second largest pollution source, demonstrating a steady contribution throughout the year, with a notable increase during the summer and fall months. The annual relative contribution of traffic constituted 25 % of the total particulate mass (PM 2.5), with monthly relative contributions varying between 6.6 and 53.1 %. Combustion of fuel and residual oil mainly comes from furnaces for heating public facilities and buildings (kindergartens, schools, hospitals), as well as in industrial facilities for heat production or some other technological processes. This source occurs consistent over the year and annual relative contribution accounted for 17% of the total particulate mass (PM 2.5) mass. Open fires and waste burning include the combustion of crop residue, agricultural and garden waste materials, as well as landfill fires and wildfires. This factor also includes the combustion of diverse waste materials in household stoves or small industrial boilers, therefore having increased contribution in the autumn and winter periods. The monthly contribution from this source comes up to 28.9 %, while the annual contribution is 11 %.

It is evident that, due to its complexity, air pollution cannot be addressed by reducing emissions from a single source, but rather by reducing emissions from all sources simultaneously. Furthermore, most air pollution problems cannot be addressed with immediate or quick steps; consequently, a continuous and comprehensive approach, supported by systematic measures, is required, with outcomes expected in the foreseeable future, based on the positive experiences of other countries.

Utilizing experiences and examples from communities that have achieved noticeable improvements is an effective strategy. In response to this urgent concern, a committed UNDP project team has compiled a comprehensive dataset highlighting innovative air protection measures worldwide. This program aims to map global air protection solutions, providing access to a diverse range of beneficial activities, policies, or strategies at local and national levels, while showcasing exemplary cases in the battle against air pollution [53].

The Polish city of Krakow, which is regarded as having some of the worst air quality in Europe, is also an excellent example. Today's scenario is entirely different thanks to the city's leadership and citizens' tenacious actions. Krakow has greatly lowered the concentrations of all pollutants and complies with today's ambient air quality standards thanks to a comprehensive program to enhance air quality that offers inhabitants both practical and financial assistance to upgrade their home heating systems [54].

Consequently, the formulation of targeted and comprehensive plans for air quality management, based on contemporary scientific evidence, along with a robust political commitment to their execution, is imperative.

## Lessons learned

| Lesson No. 1 | Solutions available |
|---|---|
| The widespread use of biomass as the primary energy source for residential heating is the predominant contributor to fine particulate matter (PM2.5) in most urban areas across the country.<br>Unfortunately, these stoves release 0.00499 tons of fine particulate matter (PM2.5) for each cubic meter of firewood combusted, clearly highlighting the problem. | Although complex, there are numerous successful examples of updating house heating systems to provide more sustainable options for home heating.<br>In densely populated areas, district or local heating systems may be the best option. In individual homes, replacing old wood stoves with exceptionally effective "air to air" or "air to water" heat pumps or natural gas boilers (if available) can virtually eliminate particulate emissions from this sector, greatly improving overall air quality and lowering the frequency of high pollution episodes in our cities.<br>Together with cost-effective heat pumps, small-scale electrical and thermal energy production plants that are more readily available, efficient, and cost-effective can offer an economically viable route out of the current situation and open the door to long-term success.<br>Nevertheless, the success of any future initiatives is based upon the development of focused and broad plans, as well as financial and practical support, strong political commitment, and public support. |
| **Lesson No. 2** | **Solutions available** |
| Traffic-related air pollution can be a significant source, contributing consistently throughout the year, with a notable increase in summer months.<br>This source encompasses vehicle exhaust emissions, mechanical wear from brakes and tires, as well as resuspended road dust. | Measures aimed at urban planning, raising awareness, and implementing clean vehicle policies and incentives form the foundation for a sustainable reduction in traffic pollution. However, these approaches often entail significant costs and require long-term commitments. In contrast, certain measures, such as traffic restrictions (including low-emission zones and car-free areas) and enhancements to public and active transportation, can be executed more quickly and effectively reduce traffic pollution. Successful strategies typically encompass a combination of actions working together. Examples include a well-expanded and improved public transport network that features frequent, reliable, and environmentally friendly buses, along with safe bike lanes, bike-sharing initiatives, park-and-ride systems located at the outskirts of the city, and congestion charges implemented in the city center, are some of the solutions that have proven effective worldwide. |

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