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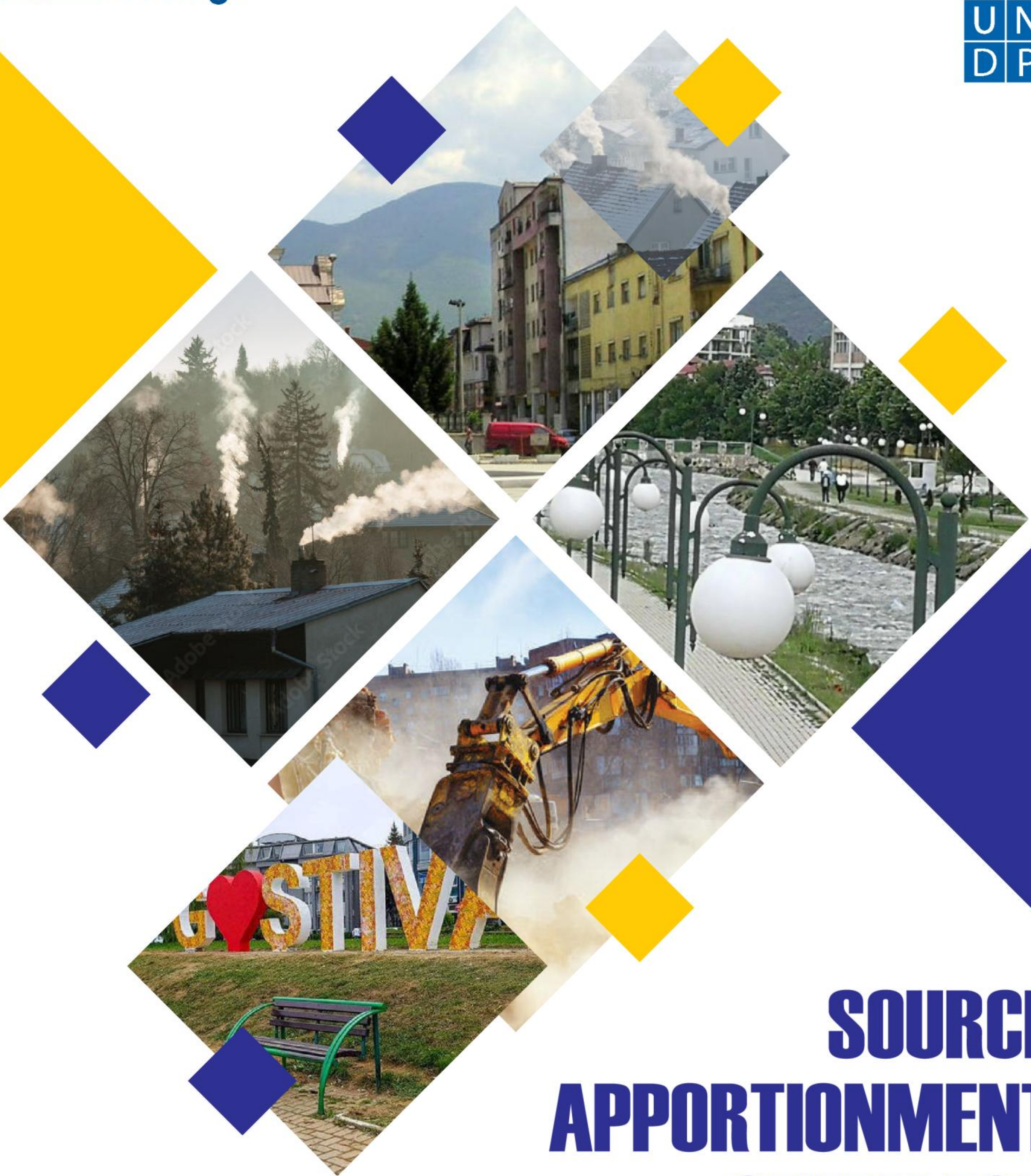

SOURCE APPORTIONMENT STUDY FOR GOSTIVAR URBAN AREA

GOCE DELCEV
UNIVERSITY
FACULTY OF NATURAL
AND TECHNICAL SCIENCES

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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Project team	
Team leader	Prof. Dr. Dejan Mirakovski – UGD FNTS
Chemical speciation and modelling	Ass. Prof. Dr. Afrodita Zendelska – UGD FNTS
QA/QC group	Prof. Dr. Marija Hadzi-Nikolova– UGD FNTS
	Prof. Dr. Blazo Boev – UGD FNTS
Laboratory process support	Prof. Dr. Tena Sijakova-Ivanova– UGD FNTS
	Ass. Prof. Dr. Ivan Boev– UGD FNTS
	Prof. Dr. Sonja Lepitkova – UGD FNTS
	Ass. Prof. Dr. Gorgi Dimov– UGD FNTS
	Ass. M.Sc. Ana Mihailovska – UGD FNTS
Technical group	M.Sc. Boban Samardziski, FNTS, AMBICON
	Igor Pavlov – FNTS, AMBICON
	Goce Bogatinov– UGD IT SG
Students' internship	Ana Marija Kostadinova
UNDP	Armen Grigoryan, Resident Representative
	Aleksandra Dimova Manchevska, Project Manager
	Dren Nevzati, Monitoring Associate
	Trajancho Naumovski, Project Assistant
Knowledge management and capacity building support	M.Sc. Pavlina Zdraveva
Communication support team	Igor Stojanov
	Elena Doneva

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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 Plan
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.

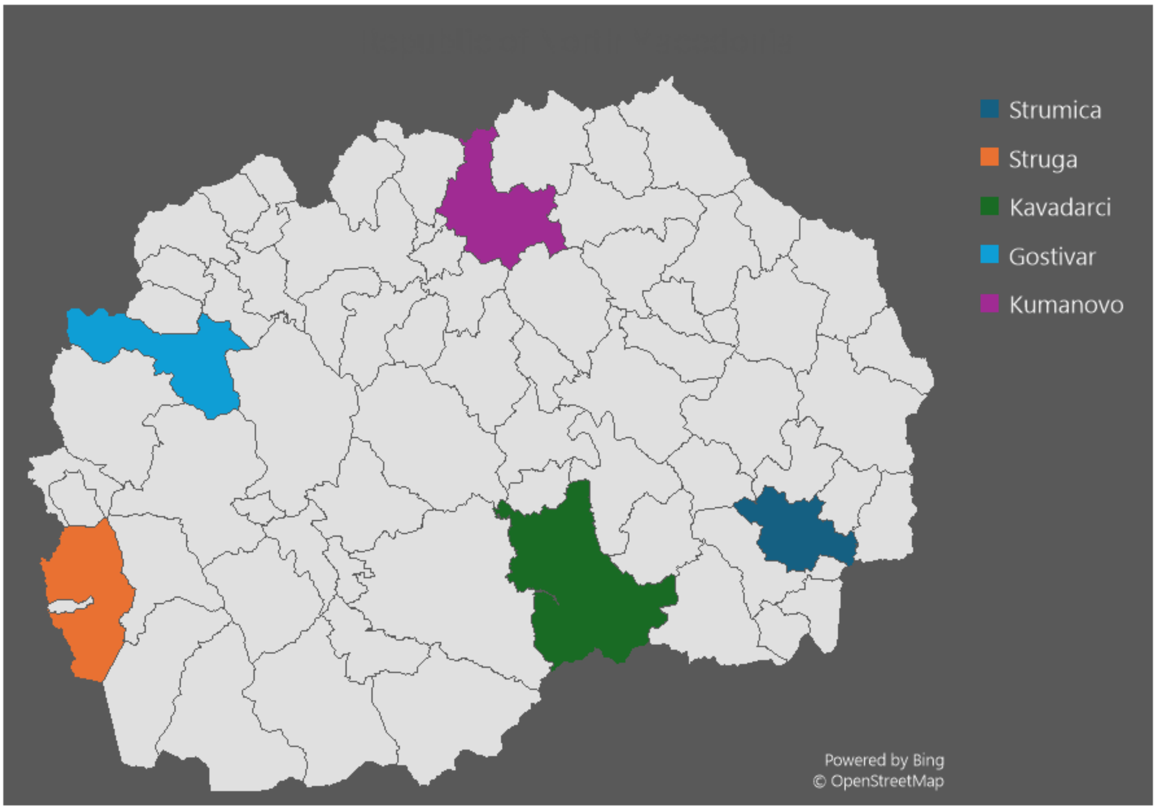


Figure 1. Map of municipalities included in this study

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. Gostivar urban area

The Municipality of Gostivar is located in the northwest portion of North Macedonia and is part of the Polog Statistical Region. The Gostivar municipality extends across the Polog plateau, more precisely at the beginning of Gorni Polog (the southernmost part of the Gostivar plain), and includes the slopes of Shar Mountain on the west side, Suva Gora on the east side, along with Bistra Mountain, the Mavrovo region, and the Gorna, Dolna, and Mala Rivers in the southwestern area of the country. It covers an area of 518.79 km^2, which is about 2.9% of the entire country.

According to the 2021 Census, Gostivar had a total population of 59,770, with 20,054 households and 27,945 apartments and houses.

Figure 2. Location of Municipalities of Gostivar

The Municipality of Gostivar is located in the Polog Valley (Goren Polog) at an altitude of 510 meters. Near Gostivar, in the village of Vrutok (5 km southwest of the city), lies the source of the largest Macedonian river, the Vardar, which flows through the city, effectively dividing it into two parts.

Additionally, nearby is the largest national park and ski resort in Macedonia, Mavrovo. Gostivar is located 67 kilometres from Skopje, and its neighbouring cities include Tetovo, 27 kilometres to the north, and Kichevo, 46 kilometres to the south [1].

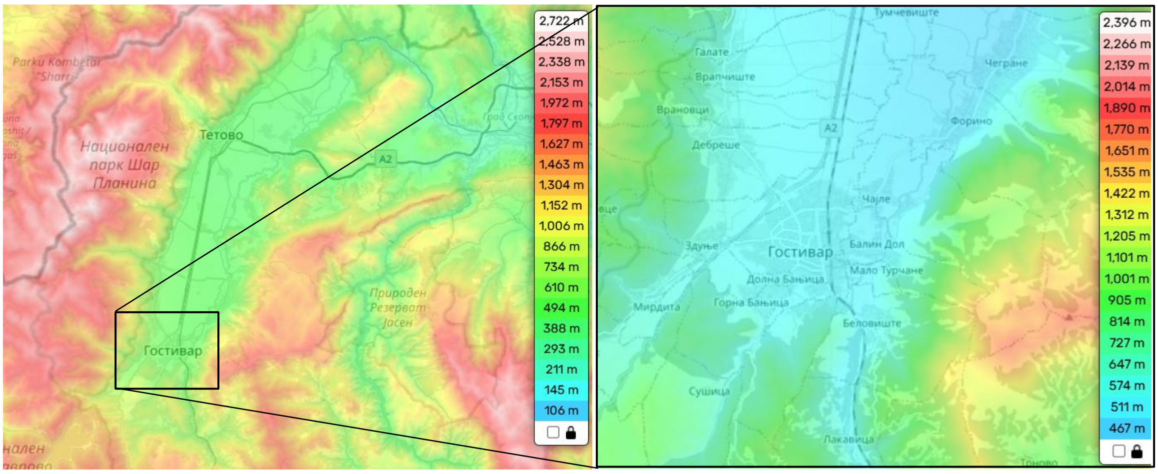


Figure 3. Gostivar topography map [2]

2.2. Climate

The average annual temperature in Gostivar is 10.6 °C. The average winter temperature is 0.7 °C, while the average summer temperature is 20.3 °C. The warmest months are July, with an average temperature of 21.1 °C, and August, with an average of 20.8 °C. The variation in average extreme temperatures is 35 °C. In contrast, the absolute extremes range within significantly wider limits, from -31 °C to +37 °C, resulting in a total variation of 68 °C. This large difference shows that the annual temperature variations in Gostivar are quite irregular, with noticeable ups and downs, typical of the temperate-continental climate in this area. Winters are notably cold, while summers are warm with pleasantly cool nights, reflecting the direct influence of the surrounding high mountain ranges [1].

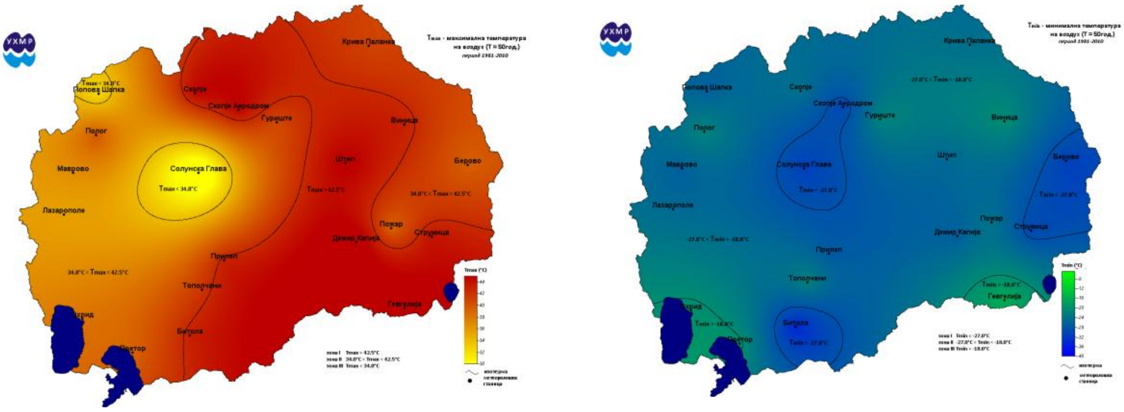


Figure 4. Maximum and minimum temperature maps for North Macedonia with probability of occurrence of 0,002 % [3]

November is the rainiest month, averaging 156 mm, while December follows with 111 mm. The spring months experience a fair amount of rain, but not as much as the autumn months. August experiences the least precipitation, along with June and July. The disparity between the rainiest November, which recorded 156 mm, and the driest August, with only 28 mm, amounts to 128 mm. This highlights the notable asymmetry in the annual precipitation distribution, with approximately 80 % derived from rain and around 20 % from snow [1].

Fog is uncommon in Gostivar, with the number of foggy days being half that of the Skopje Valley. Fog is predominantly observed in the winter months, especially in January and December, and rarely occurs during the warmer months. The average annual cloudiness in Gostivar is 5.1 tenths. The cloudiest is November with 7.2, followed by December with 7.1 tenths, i.e. the months with the most precipitation. Annually, there are approximately 105 cloudy days and around 260 bright days [1].

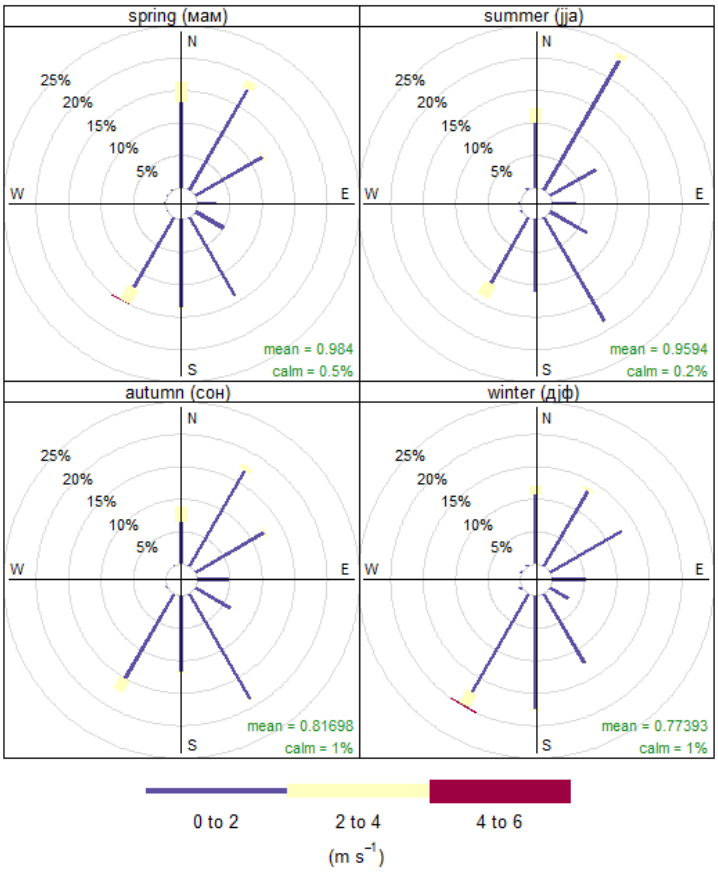


Figure 5. Seasonal wind roses during the monitoring period (March 2023 to February 2024, AMBICON Lab).

The northeast and southwest winds are the most common, at 17 % and 16 %, respectively. Among other directions, the north accounts for 13 % and the south for 14 %, both of which are quite noticeable. Gostivar is characterized by frequent winds. During the summer, southeast winds prevail, closely followed by northeast winds. The wind speeds in Gostivar are moderate, averaging 0-2 m/s, with unstable weather conditions leading to speeds of 2 to 4 m/s and occasional higher speeds exceeding 6 m/s. The nearby mountain ranges influence the weather in this city throughout the year [1].

2.3. Transportation and energy infrastructure

Gostivar is connected to the country's transport system via a well-developed road network. The following major routes pass through the municipality of Gostivar: the main road M-4 (Skopje-Ohrid), which includes a highway from Skopje via Tetovo to Gostivar, and the regional road connecting Gostivar to Debar and Ohrid. Additionally, the Skopje-Kichevo railway runs through the municipality of Gostivar.

In comparison to 2021, when a total of 11518 vehicles were registered, there were significantly more vehicles registered in Gostivar in 2023 (18253). The figure below illustrates the count of various vehicle types registered in Gostivar from 2021 to 2023, along with the classification of the vehicle fleet based on the types of fuel used [4].

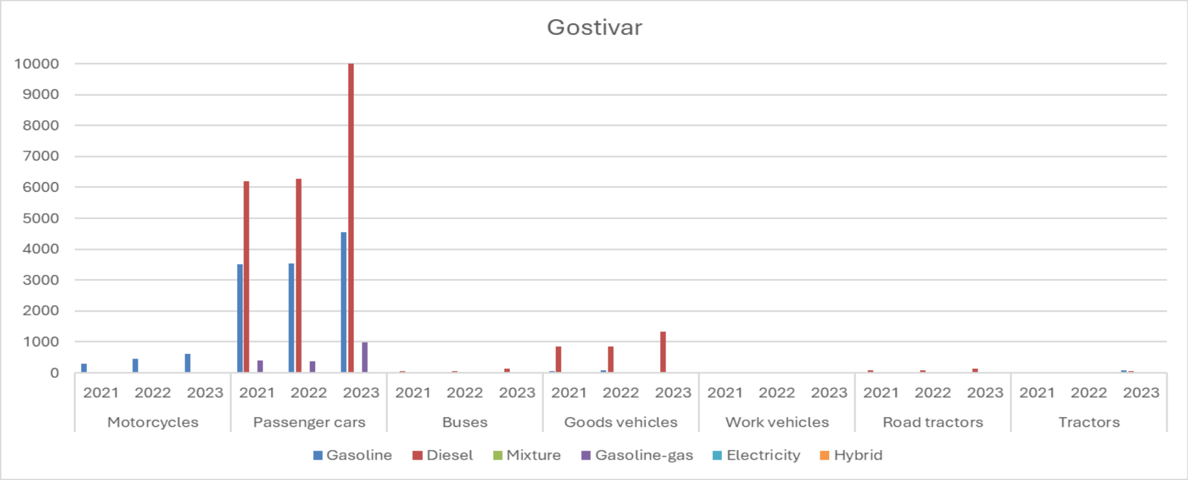


Figure 6. Number of registered vehicles in Gostivar classified according to the type and fuel used

The national power network supplies the largest portion of the municipality's electricity. In urban centers like Gostivar, the network is cable-based and operates at 20 kV, whereas the other outlets in hilly, mountainous, and lowland areas are primarily aerial. Renewable sources are also present, including several large and small hydropower plants, as well as multiple small and medium photovoltaic power stations. In the city of Gostivar, numerous 10 kV outlets are fed by the 110/20/10 kV Gostivar substation.

A 77-kilometer segment of the Skopje-Tetovo-Gostivar gas pipeline is currently under construction as part of the national strategic commitment to integrate natural gas into the energy framework. The gasification of the municipality of Gostivar has the potential to significantly reduce air pollution emissions, thereby enhancing air quality [5, 6].

2.4. Industry and service providers

The business entities located within the Municipality of Gostivar that possess installations with an integrated A permit include Swiss Method, Vardar Dolomiti, Pelagonija AD, and Progress 1998. Additionally, the businesses with integrated B permits in the Municipality of Gostivar are Quarry and Separation Silica-Rudnik Chajle, AD KEM, Quarry and Separation S-Petrol, Quarry and Separation Jefuta Engineering, Poultry Farm Nova Trgovija, Shan Kom Fix, Concrete Base El Trans, and Quarry Argjent.

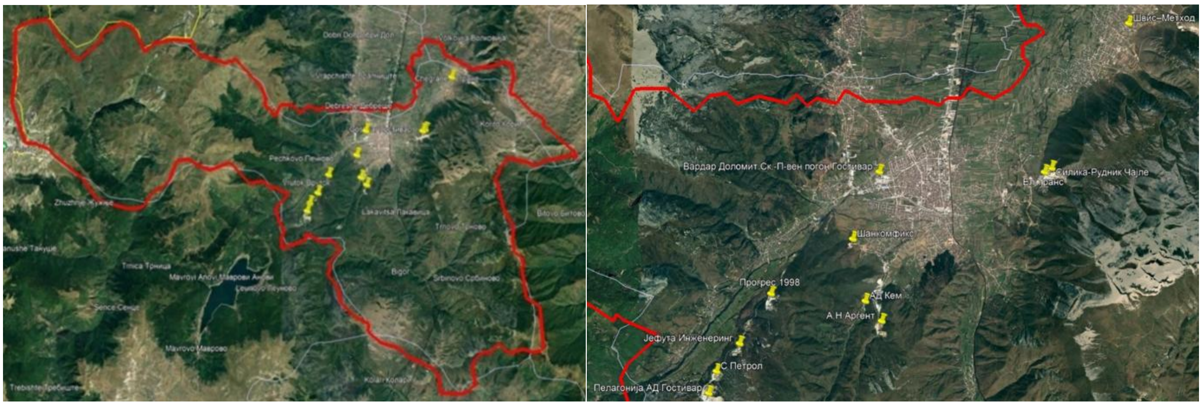


Figure 7. Sites with integrated pollution prevention permits [1]

Service providers that operate small or medium combustion plants primarily for heating purposes can also significantly affect urban air quality, as many utilize outdated units fuelled by fuel or residual oil, and in some instances, solid fuels such as wood.

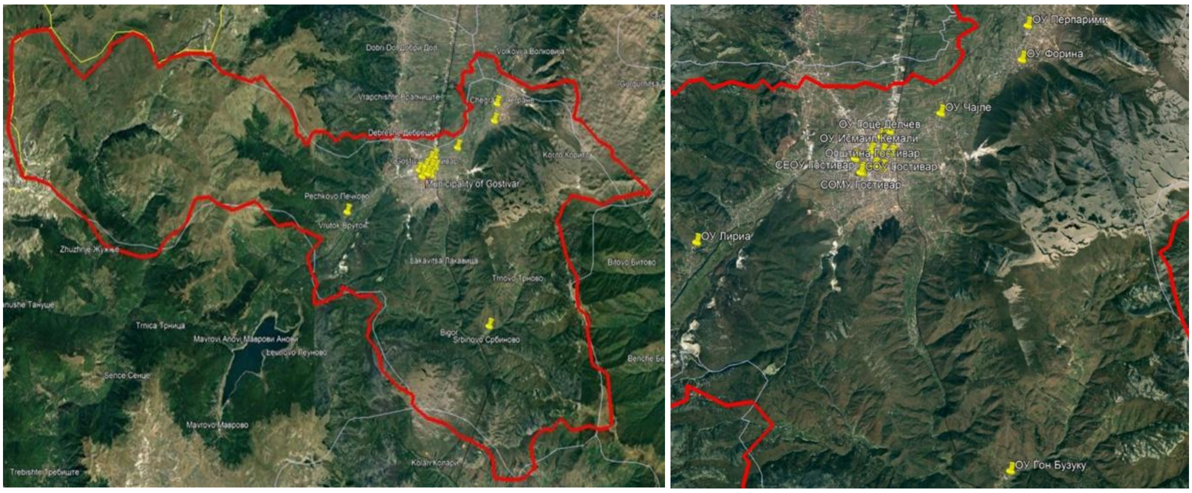


Figure 8. Service providers within Gostivar urban area [1]

2.5. Historical data on ambient air quality

The most recent air quality assessment in Gostivar municipality was performed as a part of the 2022 Air Quality Improvement Plan, utilizing data from the state monitoring network covering the period from 2018 to 2021[1]. All the information was examined and compared to the set limits in the rules about acceptable levels of pollutants in the air, which include warning levels, deadlines for meeting these limits, and long-term goals (Official Gazette of the Republic of Macedonia No. 50/05, 4/13, 183/17).

Data from the Gostivar urban monitoring station show that levels of air pollutants like nitrogen dioxide, carbon monoxide, and sulfur dioxide stayed within the limits set by national rules, indicating that these pollutants are not a major concern.

Average annual concentrations of SO_2 ranged from 1.73 to 2.70 µg/m^3, significantly lower than the allowed level of 20 µg/m^3 for ecosystem protection, and no reported exceedances of the hourly and daily SO_2 limits for human health protection.

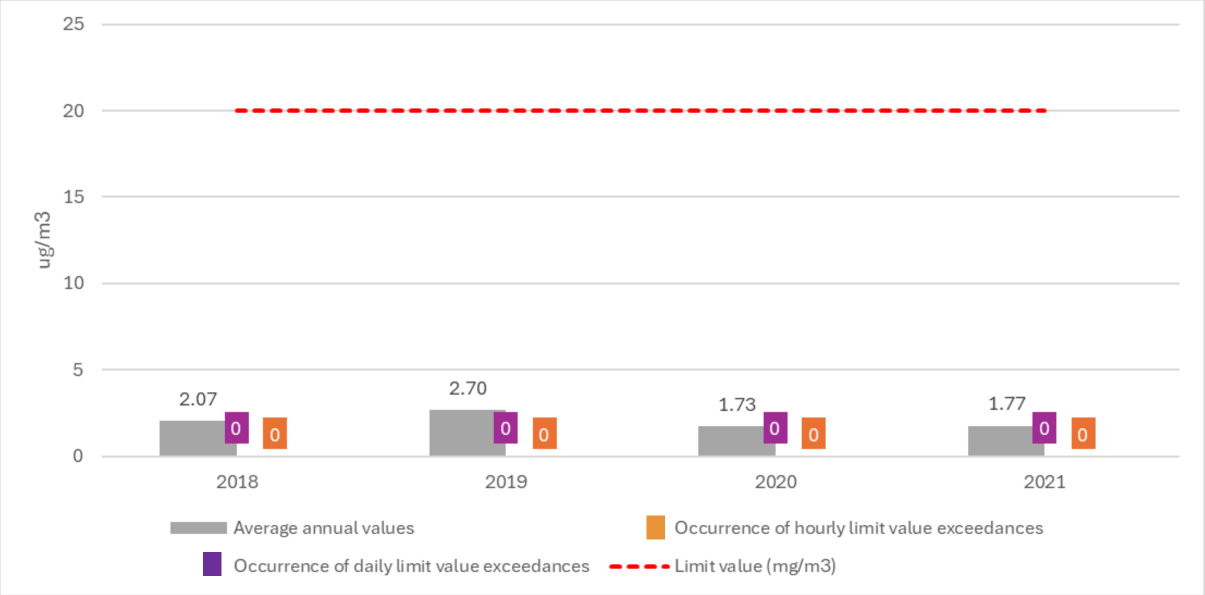


Figure 9. Average annual concentration of SO_2 from 2018 to 2021 [1]

Also, the average yearly concentrations of NO_2 range from 14.21 to 18.80 µg/m^3, well below the established annual limit value of 40 µg/m^3. Furthermore, throughout the specified period, the hourly threshold values established for the protection of human health (set at 200 µg/m^3) were not exceeded.

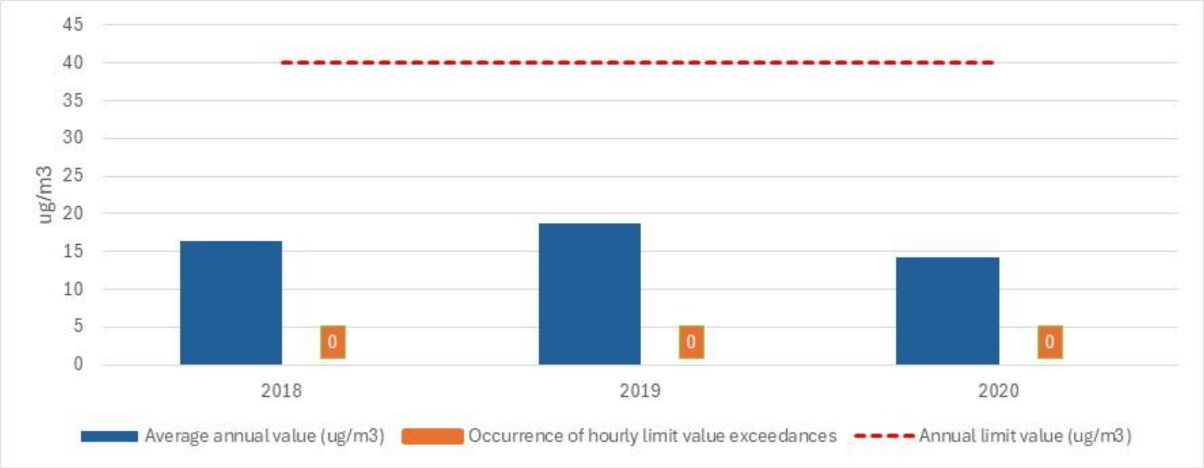


Figure 10. Average annual concentrations of NO_2 from 2019 to 2021 [1]

Carbon monoxide (CO) is similarly regarded as non-critical, as there were no cases of exceeding the health protection target value of 10 mg/m^3 during the specified time period.

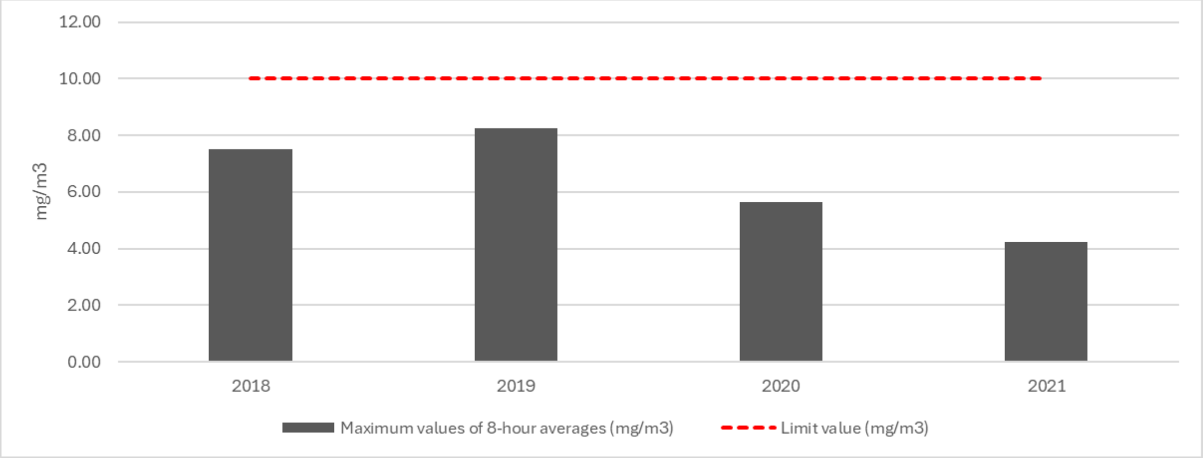


Figure 11. Maximum 8-hour averages of CO from 2018 to 2021 [1]

However, the levels of particulate matter (PM10) and ozone (O3) consistently exceed the established threshold limits. The ozone data shows that during the review period, the safe limit for protecting human health, which is 120 µg/m^3, was exceeded in 2019 and 2021, with highest 8-hour average daily ozone levels reaching 127.33 µg/m^3 and 132.65 µg/m^3, respectively. These average 8-hour maximum values were measured on July 7, 2019, and July 13, 2021. The target value for health protection of 120 µg/m^3 was exceeded twice in 2019, while 24 exceedances were noted in 2021. The observed exceedances ranged from approximately 21% to only 1% above the limit value, and while these increases may seem marginal, some studies have indicated that ozone levels below these thresholds can still pose elevated mortality risks [7]. Furthermore, studies have demonstrated the adverse effects of lower ozone levels (as low as 40 ppb) on vegetation and agricultural crops [8, 9].

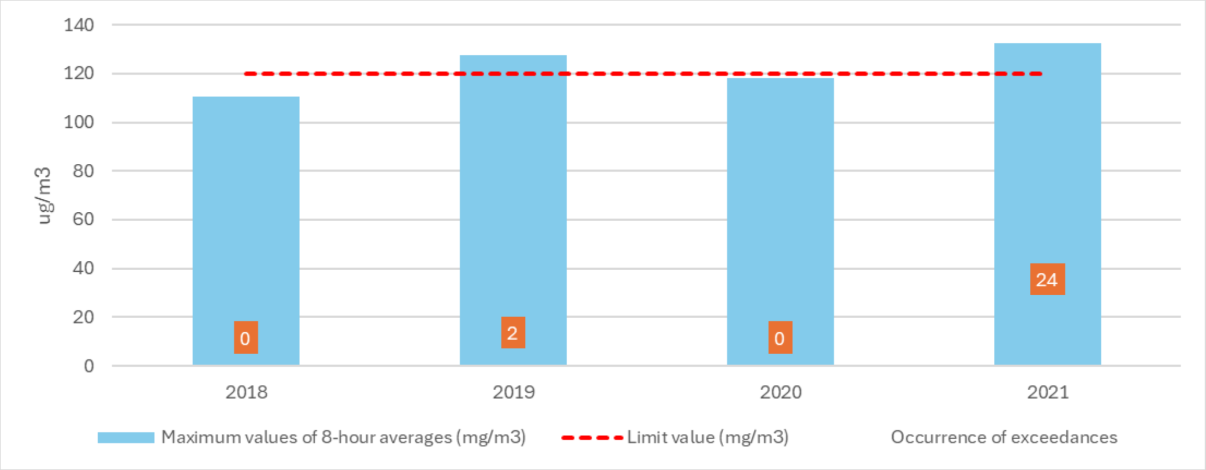


Figure 12. Maximum 8-hour averages of O3 from 2018 to 2021 [1]

The situation with suspended particulate matter is even worse, since the number of exceedances of the 24-hour limit value and average annual PM10 concentrations in Gostivar from 2018 to 2021 are consistently higher than the recommended standards.

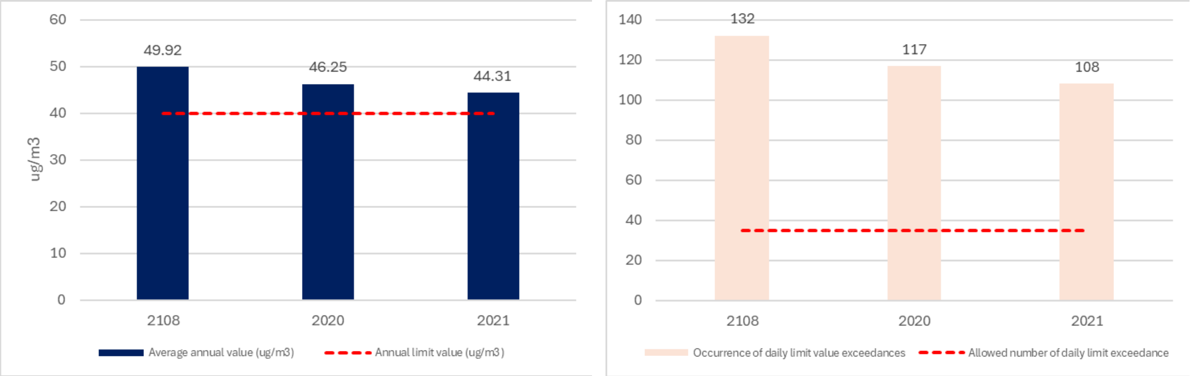


Figure 13. Average annual PM10 concentrations and frequency of exceedances of the 24-hour limit value

As seen above, the total number of 24-hour limit exceedances over a calendar year ranges from 108 to 132, which is significantly higher than the recommended threshold of 35 days. The annual limit value for human health protection has also been exceeded every year, fluctuating between 44.31 μg/m^3 in 2021 and 49.92 μg/m^3 in 2018.

Data for PM 2.5 were available only for 2021, and the average annual value recorded was 24.87 μg/m^3, slightly below the limit value set at 25 μg/m^3.

3. Major emission sources

Emission data and corresponding source profiles were compiled using several relevant sources, including the Gostivar 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] 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), 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 Gostivar municipality [1]

	Pollutants (t/year)							
	NO_x	CO	NMVOC	SO_x	NH_3	TSP	PM10	PM 2.5
Industrial process	58.99	16.01	145.44	54.31	/	1873.78	559.62	114.27
Administrative facilities	5.72	2.10	0.57	1.75	0.02	0.50	0.50	0.44
Households	14.10	1076.55	161.30	3.89	18.78	214.94	204.18	198.81
Traffic	180.99	111.16	34.40	16.64	/	15.60	12.70	10.32
Waste	0.48	8.45	31.99	0.02	/	0.71	0.68	0.63
Agriculture	41.86	/	89.17	/	250.17	35.49	11.24	4.30

The aforementioned data indicates that the manufacturing, residential, transportation, and agricultural sectors are the Municipality of Gostivar's primary sources of emissions.

The manufacturing industry sector contributes 87.52 % to the annual emissions of total suspended particles (TSP) in the Municipality of Gostivar, whereas the residential sources sector accounts for 10.04 %. This sector is also dominant contributor to SO_x and PM10, while also significantly contributing to NO_x and NMVOC emissions.

The residential sector (households) is the largest source of CO and PM2.5 emissions and significantly contributes to NMVOC and PM_{10} emissions. The traffic sector is the primary source of NO_x emissions and also significantly contributes to CO and SO_x emissions. NH_3 emissions predominantly arise from the agricultural sector.

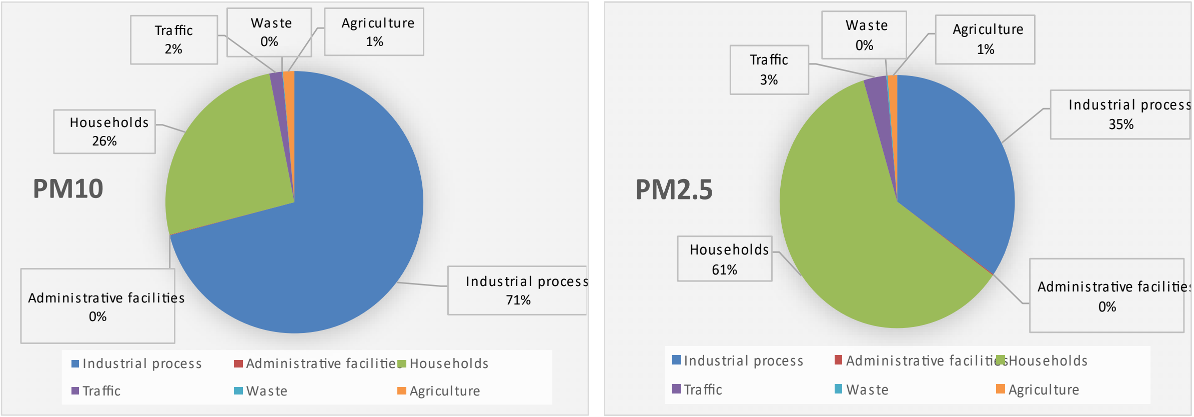


Figure 14. Sectoral contribution to particulate mater emissions [1]

Industrial operations and residential heating are the primary sources of particulate matter emissions, with industry responsible for 71% of PM10 emissions and residential heating for 61% of PM2.5 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.

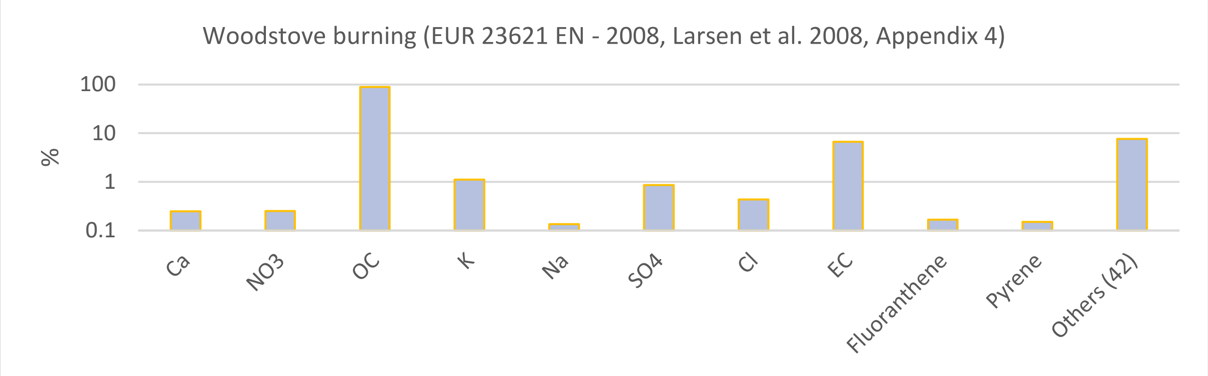


Figure 15. Woodstove burning chemical profile (closed fireplace)

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.

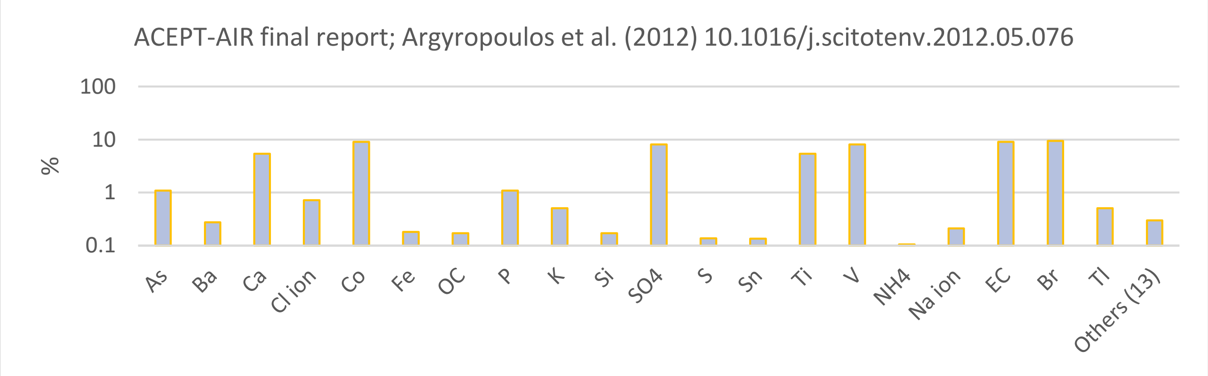


Figure 16. Open burning of crop residues chemical profile

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.

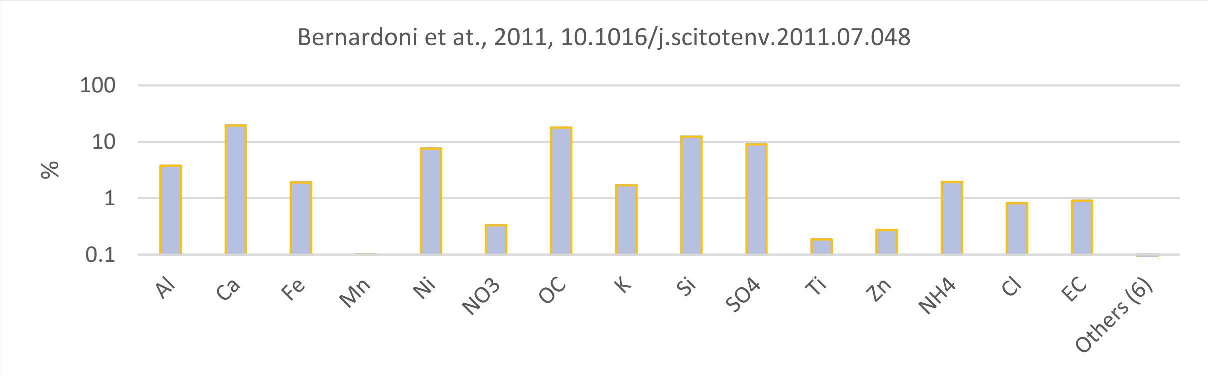


Figure 17. Construction activities chemical profile

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.

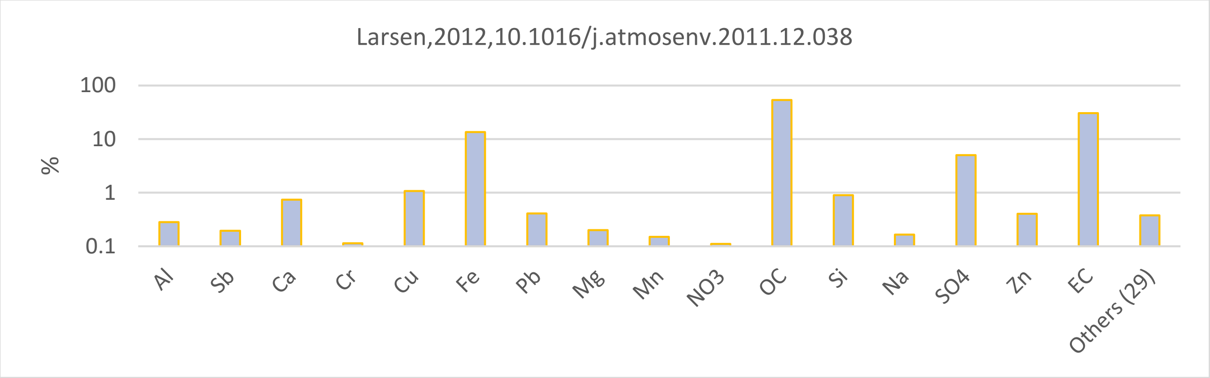


Figure 18. Exhaust diesel and gasoline chemical profile

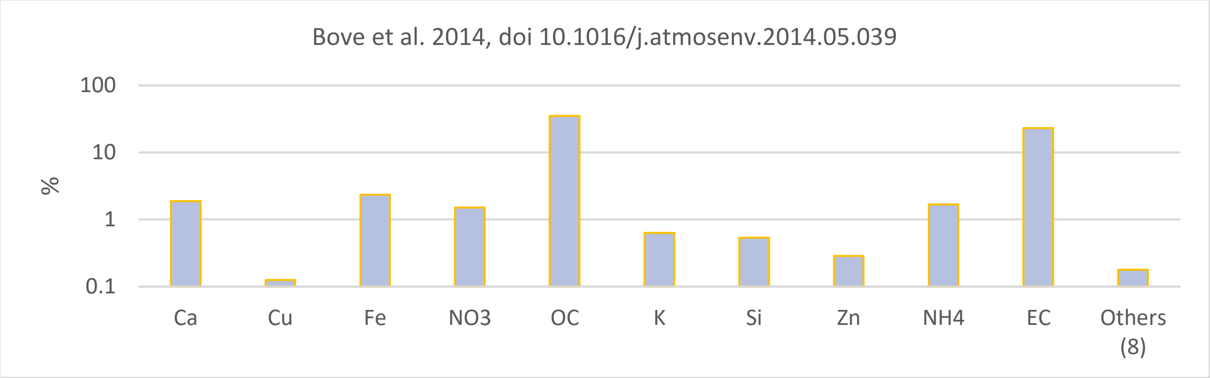


Figure 19. Urban traffic chemical profile

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.

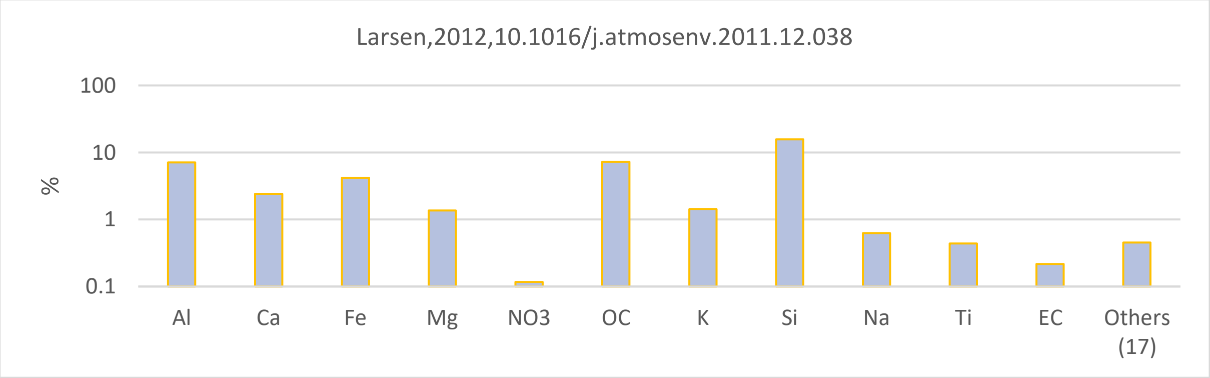


Figure 20. Road dust chemical profile

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.

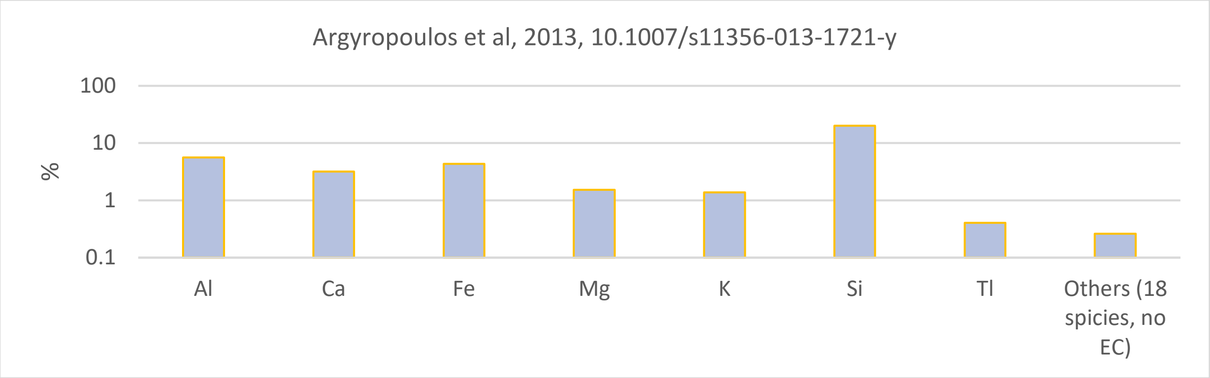


Figure 21. Soil dust chemical profile

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 %).

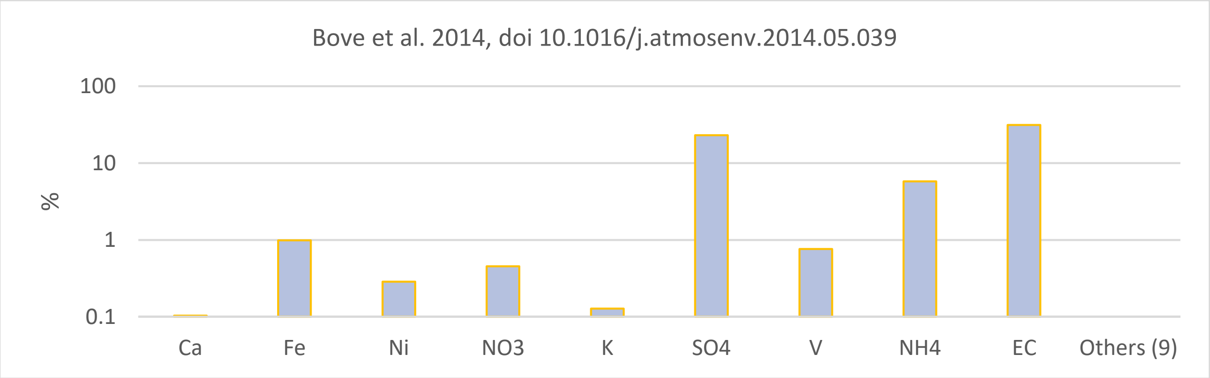


Figure 22. Residual oil chemical profile

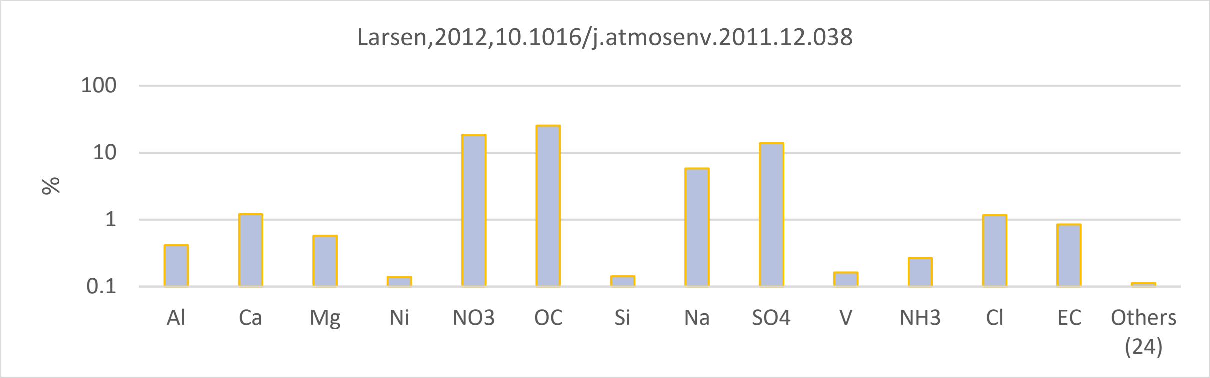


Figure 23. Fuel oil chemical profile

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

Considering the SA study goals, current data availability, as much as the project document requirements, one specific receptors/sampling points was selected and set within the urban regions of Gostivar.

The sampling point in Gostivar, integrated with the state monitoring network (our code MP5-AQP), is situated at the premises of the "Goce Delchev" Primary School.

GPS coordinates: Y - 7.492.502 X - 4.627.539

Figure 24. Monitoring location in Gostivar urban area

The sampling program at this site commenced on March 4, 2023. A 24-hour sample was collected every other day. A total of 191 samples were collected in Gostivar from March 4, 2023, to March 26, 2024.

All QA/QC processes for filter conditioning, handling, and storage were executed in accordance with the Standard Operating Procedure of the UGD AMBICON Lab, which is ISO 17025 accredited 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.

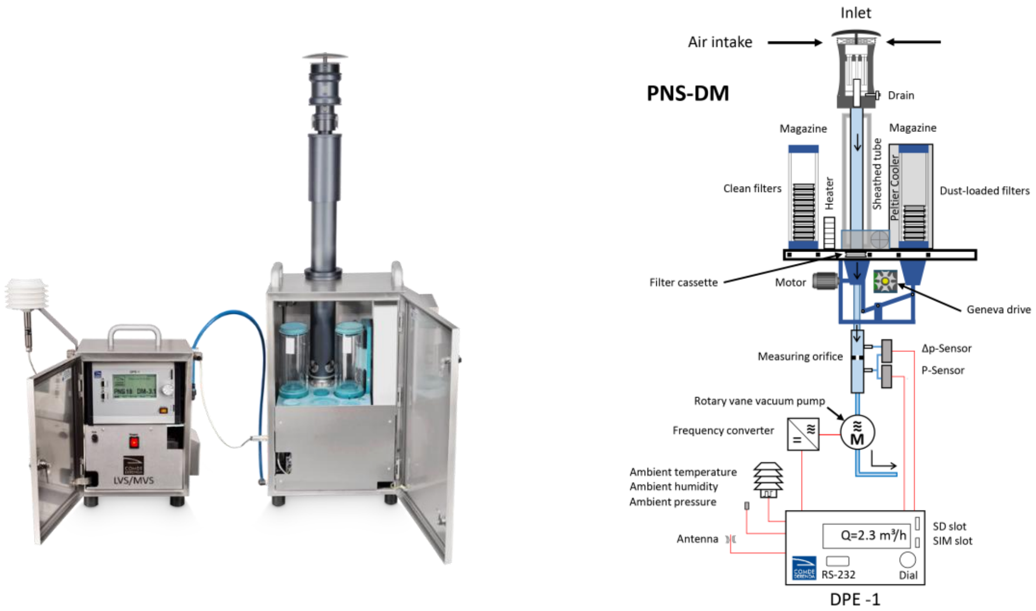


Figure 25. Sequential sampling system PNS 18T-DM 6.1

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].

Analyses were carried out in the AMBICON Lab, at Goce Delchev University in Shtip, 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.

Figure 27. NEX CG by Rigaku

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
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

Element	Certified reference concentration (ng/cm^2)	Average	Standard deviation	Coefficient of variation (%)	Recovery (%)
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 below.

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: $|z| \leq 2.0$ the result is considered acceptable $2.0<|z|<3.0$ indicate a warning signal $|z|\geq 3.0$ 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 Gostivar, 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 helps us to summarize, describe and illustrate the data in a more meaningful fashion, making data interpretation easier. Therefore, a summary of descriptive coefficients for data sets collected for each of the sites included in the monitoring program is given below.

Descriptive statistical analysis presented, include both categories: measurements of central tendency and measures of variability (or variation).

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

Measures of variability are a means of summarizing a set of data by indicating how widely the results observed are distributed. Several statistics to explain this spread are used, including minimum, maximum, quartiles, variance, and standard deviation.

Descriptive coefficients are combined with tabular and graphical descriptions, as much as the comments and discussion of the results.

In addition, a correlation matrix illustrating relationship between all values in the dataset is also given, as a basic tool for summarizing massive datasets and identifying and visualizing data relations.

The corelation matrix table contain the correlation coefficients between each variable based on Pearson parametric correlation test and its colour coded for correlation values above ± 0.6.

In this specific case, correlation matrixes present relationships between the species, indicating their common sources, but also serves as an input for exploratory factor analysis and data quality control.

Table 5. Statistical evaluation – Gostivar dataset

	Units	N	Mean	SD	Minimum	Maximum	C.V.	95 th %	5 th %
$PM_{2,5}$	µg/m^3	174.0	29.1	19.0	4.7	153.1	65.3	58.3	10.5
Na	ng/m^3	174.0	13.4	25.5	5.4	168.5	191.2	54.6	5.5
Mg		174.0	20.7	21.2	0.6	124.2	102.3	55.9	0.7
Al		174.0	103.4	110.0	0.5	785.2	106.4	261.2	0.5
Si		174.0	317.8	314.1	0.3	2120.7	98.8	751.4	6.9
P		174.0	1.6	1.2	0.0	6.5	75.7	3.4	0.0
S		174.0	94.7	59.5	0.2	322.2	62.8	198.1	14.7
Cl		174.0	24.5	42.0	0.2	278.0	171.5	98.4	0.2
K		174.0	169.1	137.4	2.1	930.0	81.3	448.5	38.4
Ca		174.0	973.2	914.5	1.5	6720.8	94.0	2415.5	53.3
Ti		174.0	20.4	18.6	1.1	119.7	91.3	48.9	1.8
V		174.0	2.3	2.3	0.6	14.8	99.6	6.0	0.6
Cr		174.0	0.6	0.5	0.4	4.4	84.4	1.4	0.5
Mn		174.0	6.2	4.7	0.5	31.1	76.2	12.8	1.2
Fe		174.0	188.9	178.0	0.2	1209.7	94.2	424.6	11.9
Co		174.0	11.1	8.9	0.4	64.5	80.2	24.3	2.3
Ni		174.0	2.3	2.0	2.1	28.3	85.5	2.3	2.1
Cu		174.0	4.3	5.9	1.9	76.4	138.3	7.9	1.9
Zn		174.0	18.8	79.7	2.2	1047.9	423.7	29.8	2.2
As		174.0	0.5	0.2	0.2	1.3	48.0	1.0	0.2
Se		174.0	2.0	0.9	1.5	5.1	45.3	3.9	1.5
Br		174.0	1.5	0.7	0.7	3.6	44.4	2.7	0.7
Rb		174.0	1.7	0.9	0.6	4.5	55.7	3.3	0.6
Sr		174.0	9.5	5.8	0.0	22.8	61.9	18.1	1.0
Zr		174.0	3.0	2.0	0.0	10.4	65.7	5.9	0.2
Mo		174.0	1.1	0.7	0.0	3.7	62.5	2.3	0.2
Cd		174.0	0.7	0.5	0.0	3.6	79.0	1.7	0.2
Ba		174.0	24.1	22.2	1.3	143.1	91.8	57.9	1.3
Pb		174.0	8.0	5.8	3.7	55.8	72.8	15.8	3.7
EC		174.0	8466.0	5811.4	302.0	32288.0	68.6	20025.8	1811.0
NH_4		174.0	411.8	322.6	9.1	1772.3	78.3	1047.1	54.4
SO_4		174.0	2388.1	2548.9	9.1	20422.6	106.7	4942.6	272.5
NO_3		174.0	485.9	766.4	9.0	4411.6	157.7	2142.6	9.1

Table 6. Corelation matrix – Gostivar 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	0.33	1.00																															
Mg	0.23	0.67	1.00																														
Al	0.21	0.62	0.97	1.00																													
Si	0.21	0.63	0.98	0.99	1.00																												
P	0.19	0.56	0.91	0.89	0.91	1.00																											
S	0.20	0.09	0.29	0.27	0.27	0.45	1.00																										
Cl	0.39	0.61	0.16	0.09	0.10	0.13	0.07	1.00																									
K	0.57	0.48	0.31	0.27	0.27	0.23	0.25	0.64	1.00																								
Ca	0.24	0.72	0.90	0.84	0.88	0.84	0.19	0.24	0.32	1.00																							
Ti	0.24	0.65	0.97	0.98	0.99	0.88	0.25	0.14	0.32	0.89	1.00																						
V	0.23	0.64	0.95	0.96	0.96	0.84	0.22	0.12	0.30	0.86	0.97	1.00																					
Cr	0.24	0.62	0.81	0.84	0.82	0.65	0.14	0.08	0.28	0.66	0.82	0.82	1.00																				
Mn	0.26	0.66	0.95	0.95	0.96	0.89	0.24	0.16	0.33	0.93	0.96	0.93	0.78	1.00																			
Fe	0.24	0.63	0.97	0.99	0.99	0.89	0.25	0.10	0.28	0.87	0.99	0.96	0.83	0.97	1.00																		
Co	0.22	0.58	0.95	0.98	0.97	0.86	0.22	0.07	0.27	0.82	0.97	0.95	0.85	0.95	0.99	1.00																	
Ni	0.12	-0.03	-0.08	-0.08	-0.08	-0.11	-0.11	-0.05	0.00	-0.08	-0.07	-0.06	0.10	-0.03	-0.02	0.01	1.00																
Cu	0.21	0.01	-0.06	-0.06	-0.07	-0.07	-0.04	0.00	0.04	-0.06	-0.05	-0.04	0.11	-0.01	-0.01	0.02	0.92	1.00															
Zn	0.18	0.02	-0.08	-0.08	-0.09	-0.11	-0.09	0.07	0.08	-0.08	-0.07	-0.06	0.10	-0.02	-0.03	0.01	0.97	0.92	1.00														
As	0.27	0.03	0.04	0.04	0.05	0.09	0.13	0.17	0.18	0.06	0.06	0.04	0.04	0.09	0.08	0.09	0.18	0.17	0.21	1.00													
Se	-0.10	-0.04	-0.07	-0.05	-0.06	-0.02	-0.15	0.04	-0.08	-0.09	-0.07	-0.07	0.02	-0.06	-0.06	-0.01	-0.03	-0.06	-0.01	0.25	1.00												
Br	0.23	0.01	0.02	0.03	0.04	0.07	0.10	0.13	0.13	0.02	0.05	0.03	0.03	0.07	0.06	0.09	0.15	0.15	0.19	0.92	0.27	1.00											
Rb	0.15	-0.02	-0.06	-0.02	-0.04	-0.07	-0.17	0.05	0.16	-0.12	-0.03	-0.01	0.13	-0.02	-0.02	0.09	0.18	0.15	0.21	0.32	0.40	0.41	1.00										
Sr	-0.08	-0.09	0.00	0.05	0.03	-0.02	-0.19	-0.11	-0.08	-0.12	0.02	0.04	0.19	0.00	0.03	0.17	0.17	0.13	0.18	0.22	0.45	0.30	0.81	1.00									
Zr	0.18	0.50	0.85	0.82	0.85	0.99	0.55	0.13	0.23	0.78	0.82	0.77	0.59	0.83	0.82	0.80	-0.11	-0.08	-0.12	0.10	-0.02	0.08	-0.06	-0.01	1.00								
Mo	0.20	0.09	0.29	0.27	0.27	0.45	1.00	0.07	0.25	0.19	0.25	0.22	0.14	0.24	0.25	0.22	-0.11	-0.04	-0.09	0.13	-0.15	0.10	-0.17	-0.19	0.55	1.00							
Cd	0.56	0.48	0.32	0.30	0.29	0.24	0.23	0.63	0.99	0.33	0.34	0.33	0.31	0.35	0.30	0.30	0.01	0.04	0.09	0.19	-0.05	0.15	0.23	0.01	0.24	0.23	1.00						
Ba	0.24	0.65	0.97	0.98	0.99	0.88	0.25	0.14	0.32	0.89	1.00	0.97	0.82	0.96	0.99	0.97	-0.08	-0.06	-0.07	0.06	-0.07	0.05	-0.02	0.03	0.82	0.25	0.34	1.00					
Pb	0.37	0.06	-0.09	-0.09	-0.10	-0.07	-0.05	0.42	0.21	-0.10	-0.08	-0.09	-0.01	-0.06	-0.07	-0.01	0.16	0.21	0.25	0.29	0.31	0.32	0.49	0.41	-0.04	-0.05	0.25	-0.08	1.00				
EC	0.17	-0.16	-0.02	0.03	0.01	-0.05	-0.06	-0.23	-0.11	-0.09	0.00	-0.01	0.08	0.04	0.07	0.08	0.28	0.27	0.28	0.24	0.09	0.28	0.21	0.21	-0.07	-0.06	-0.09	0.00	0.05	1.00			
NH4	0.21	-0.21	-0.19	-0.18	-0.18	-0.01	0.68	-0.04	0.05	-0.23	-0.19	-0.20	-0.17	-0.17	-0.18	-0.16	0.05	0.10	0.09	0.25	-0.02	0.25	0.09	0.03	0.09	0.68	0.05	-0.19	0.08	0.21	1.00		
SO4	0.25	0.10	0.17	0.20	0.19	0.17	0.36	0.01	0.25	0.11	0.19	0.20	0.23	0.22	0.22	0.23	0.50	0.48	0.53	0.20	-0.12	0.19	0.13	0.10	0.19	0.36	0.25	0.19	0.05	0.23	0.39	1.00	
NO3	0.34	0.02	-0.22	-0.23	-0.23	-0.29	0.02	0.32	0.54	-0.11	-0.18	-0.18	-0.10	-0.13	-0.18	-0.19	0.17	0.19	0.25	0.25	0.00	0.18	0.18	-0.03	-0.28	0.02	0.54	-0.18	0.18	0.26	0.25	0.19	1.00

Temporal variations

Temporal variations of PM2.5 concentrations assist in clarifying the sources and contributing factors that cause air pollution [15, 16]. Diurnal and seasonal trends can differentiate among traffic-related, industrial, and meteorological impacts on PM2.5 concentrations. Detailed knowledge of PM2.5 temporal patterns can guide the development of effective air quality management strategies and policies [17]. This includes implementing targeted emission control measures, optimizing monitoring networks, and issuing timely public advisories. As the temporal variations in PM2.5 are influenced by meteorological factors, such as temperature, humidity, and wind patterns [18], understanding these relationships is essential for assessing the potential impacts of climate change on air quality.

Temporal variations are evaluated using gravimetric data alongside real-time data from collocated referent monitoring stations. Modelling was carried out using the Openair R package, designed for the analysis of air quality data, or more broadly, atmospheric composition data. The package is widely utilized in academics, as well as in the public and corporate sectors.

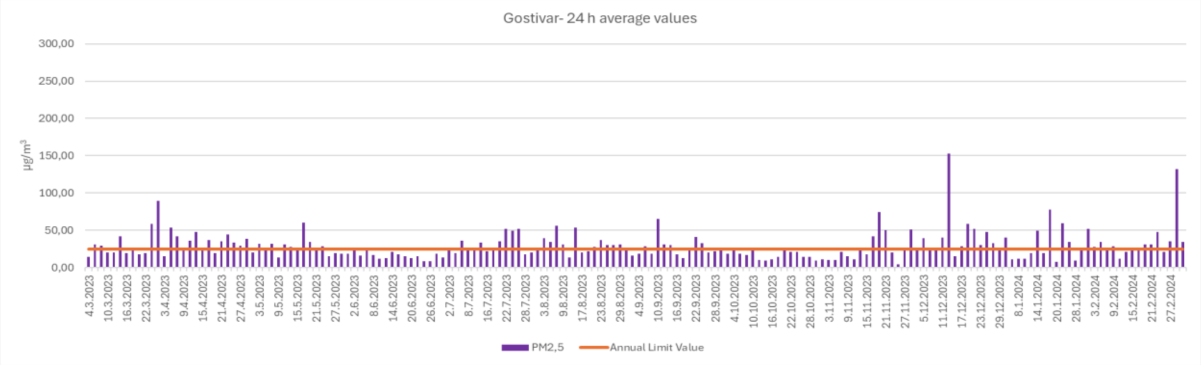


Figure 30. PM 2.5 – daily average concentrations from March 2023 to March 2024

The daily average PM2.5 concentrations measured at the Gostivar monitoring site demonstrate significant daily and seasonal variations, surpassing all national and European Union limits, targets, and thresholds established for human health protection. Daily readings displayed considerable variability, with a Standard Deviation of 19 µg/m^3 and a coefficient of variation of 65.3 %. The concentrations varied from a minimum of 4.7 µg/m^3 to a maximum of 153 µg/m^3, yielding an average annual value of 29.1 µg/m^3, which exceeds the annual threshold limit value of 25 µg/m^3 by approximately 16 %.

During the heating season, significantly higher maximum concentrations are observed; however, the average value for the months of the heating season is 30.6 µg/m^3, which is only 10 % higher than the average during the warm months. In the spring and summer months, the average concentration is 27.7 µg/m^3, also exceeding the annual limit value by approximately 10%. Alarmingly, 50 % of the days exceeded the annual limit for PM 2.5 (25 µg/m^3), with 87 out of 174 valid daily readings.

Modelled data, however, show that there is no apparent variation in particulate matter concentration by day of the week or time of day during the spring, summer, or even autumn. On the opposite side, although there are no significant differences between the days of the week, during the winter there are expressed daily variations with distinct peaks in particulate matter levels at specific times of the day (early morning and late evening). This pattern is often influenced by an interaction of meteorological factors, anthropogenic activities, and local emissions, and is predominantly attributed to the increased utilization of woodstoves and other solid fuel heating means, which discharge substantial quantities of particulate matter into the atmosphere. The morning peak typically coincides with the initiation of daily activities, such as commuting and increased heating requirements, whereas the evening peak aligns with the return home and subsequent heating activities [19].

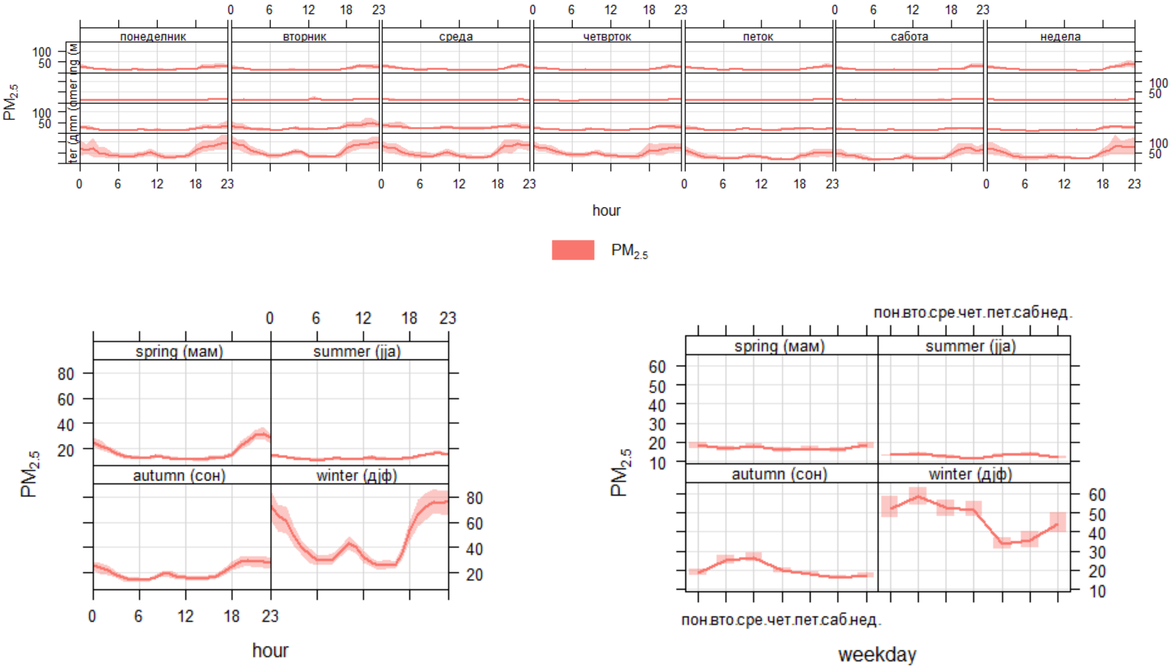


Figure 31. Daily variations in concentrations throughout all days, seasons, and weekdays

Correlation between meteorological conditions and PM concentrations

Bivariate polar plots are an effective analytical tool for understanding the origins and fluctuations of particulate matter, essecaly finer fractions like PM 2.5. These plots utilize polar coordinates to illustrate the correlation between wind speed and direction, enabling researchers to visualize the impact of these meteorological variables on PM concentrations. The radial axis (circles) commonly represents wind speed, whilst the angular axis signifies wind direction, aiding in the identification of major pollution sources according to their spatial distribution in relation to meteorological conditions.

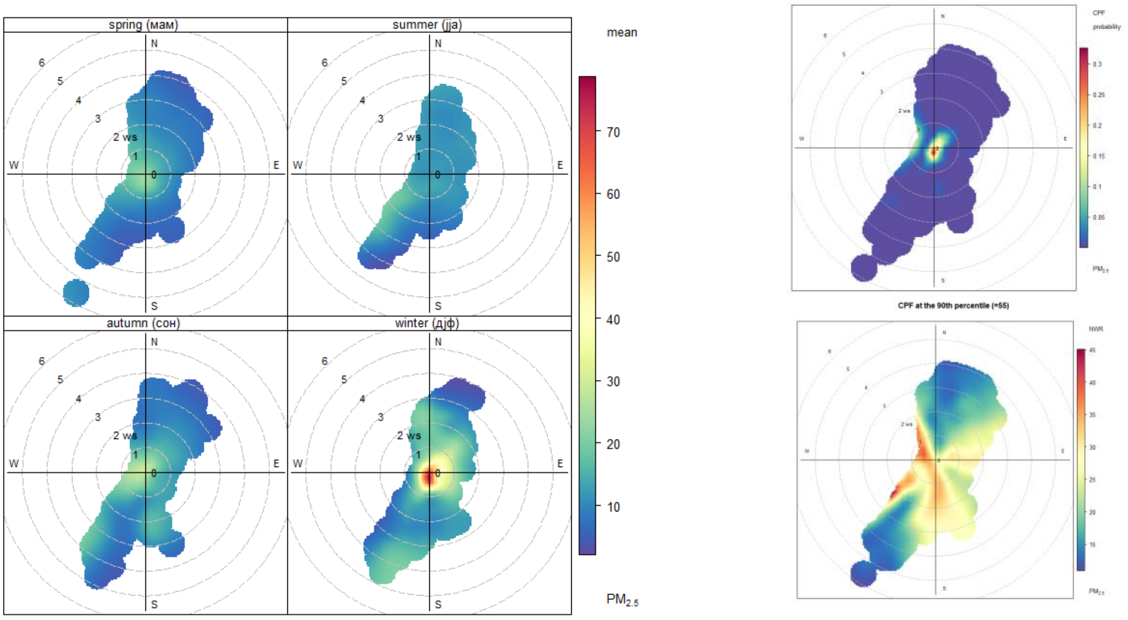


Figure 32. Bi-variate (seasonal), CPF and non paramteric polar plots

Polar plots for the Gostivar area show that changes in concentration are mainly affected by local sources, as higher PM levels are mostly seen during quiet winter weather, which usually has low wind speeds below 1 m/s. The conditional probability function supports this assertion by showing that higher particulate matter levels are mainly linked to low wind speeds, suggesting that these levels originate from local or nearby sources.

Furthermore, non-parametric wind regression (NWR) plots were employed as an alternate modelling approach to improve the understanding of the spatial distribution of pollution sources in relation to wind patterns. This methodology employs nonparametric kernel smoothers that assign weights to concentrations on a surface based on their proximity to specified wind speed and direction intervals.

Additional statistical analyses show that this relationship can be explained primarily by the location of the measuring station, which is located in the northern part of the city, but also by the position of the sources in its immediate vicinity. As we have said, high concentrations are associated only with weak winds from all directions, which indicates that the pollution is local (from the immediate vicinity). Non-parametric regression defines the northwestern part of the urban zone and the village of Debreshe, the southwestern part of the city and the villages of Dolna and Gorna Banjica as the most significant directions.

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 Gostivar is higher than the values recorded in Skopje and is within the range identified in certain regions of Southern Europe, achieving an annual average of around 6 % [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.

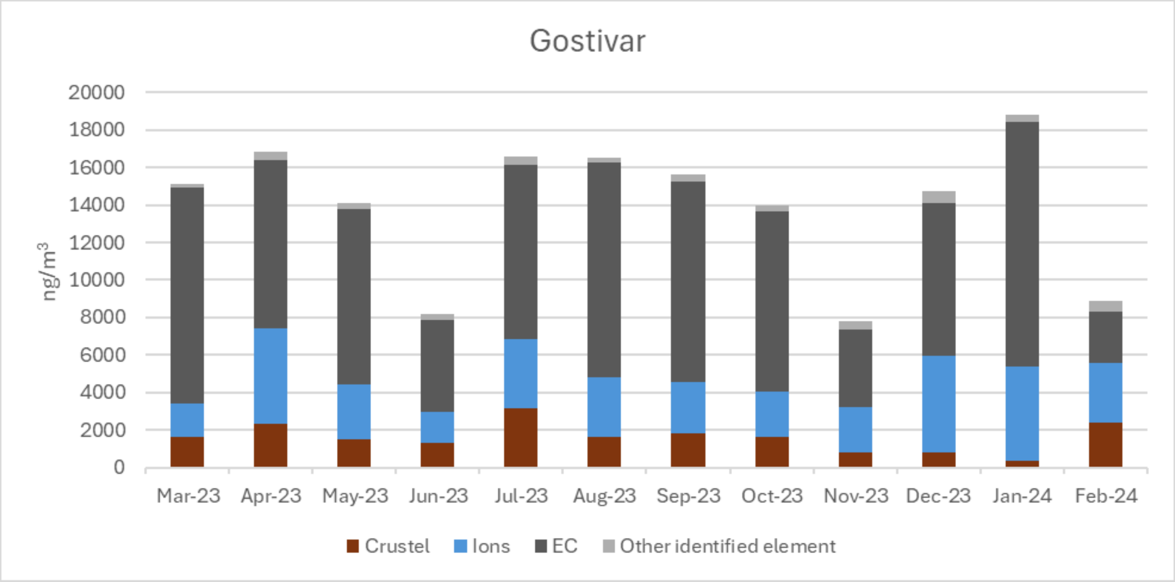
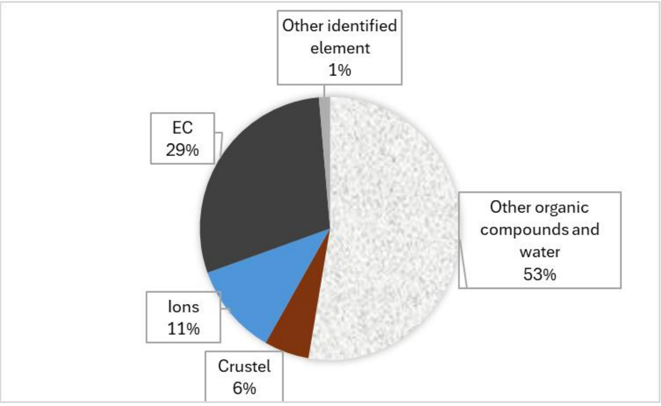


Figure 33. Major components and elemental groups identified

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 11 % 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 Gostivar exceed European averages, with an average of 29 %. This figure is higher than that observed in Skopje and values recorded in Central Europe. 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
Northwestern Europe	5	7	37
Southern Europe	11	8	22
Central Europe	5	14	32
Skopje	4	23	16
Gostivar	6	29	11

Figure 34. 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, encompassing only lead and nickel. The results for arsenic and cadmium are available; however, they are excluded from direct comparison due to significant uncertainty associated. It was determined that 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.

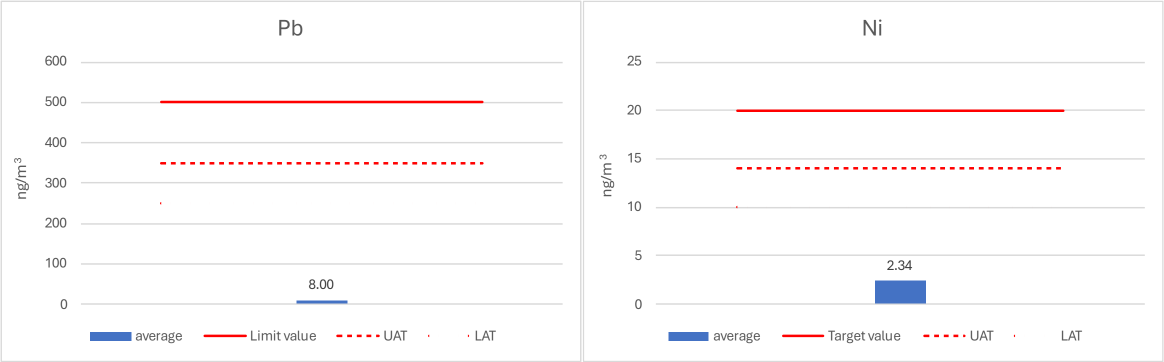


Figure 35. Average monthly concentrations of lead (Pb) and nickel (Ni) in Gostivar

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 allocation (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 ways that can be used to do this task.

Recent years have seen the rise in importance of receptor-oriented models (also known as receptor models (RMs)) in environmental sciences, which are used to elicit information from datasets that contain a number of features (chemical or physical qualities) associated with the measured samples. For example, they can be used to assess the contribution of contamination and pollutant sources in various types of samples, starting with the information provided by the samples (which is recorded at the monitoring site) and progressing to the point of effect, or receptor.

Receptor models are also known as multivariate methods because they are used to analyze a data set containing a large number of numerical values as a whole. Receptor models, to be more precise, are mathematical methodologies for measuring the contribution of sources to samples based on their composition or fingerprints. To separate impacts, the composition or speciation is identified using media-specific analytical methods, and key species or combinations of species are required. 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.

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

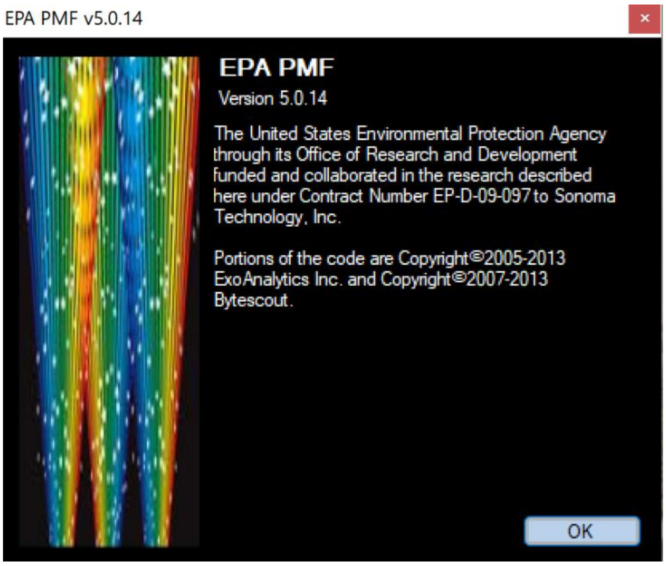
A dataset containing a vast amount of data consisting of chemical elements (such as elemental concentrations) acquired from a large number of observations (samples) is required to find the answer. The larger the data matrix, the more likely the model is to uncover separate factors that can be used as 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 36. 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, basic statistics tests including dispersion, distribution, correlation matrices, linear regression and time trends were performed in order to examine the relationships between 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 first treated to remove values that potentially decrease the analysis quality. To validate the data and uncover values that were out of the usual when compared to the rest of the dataset, scatter plots and time series analysis were utilized. After data validation, original datasets included 32 species and 174 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 Gostivar datasets included 5 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 Gostivar are as follows: biomass burning, traffic, road and soil dust, open fire and waste burning and secondary aerosols.

Biomass burning incorporates emissions from different types of woodburning stoves and boilers used mostly in residential heating. Key species found is 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 be emitted from other sources, such as soil dust [38], K has been used extensively as an inorganic tracer to apportion biomass burning contributions to ambient aerosol and was associated with biomass burning in PMF source profiles in Tirana, Skopje, Athens, Belgrade, Banja Luka, Debrecen, Chisnay, Zagreb and Krakow [39].

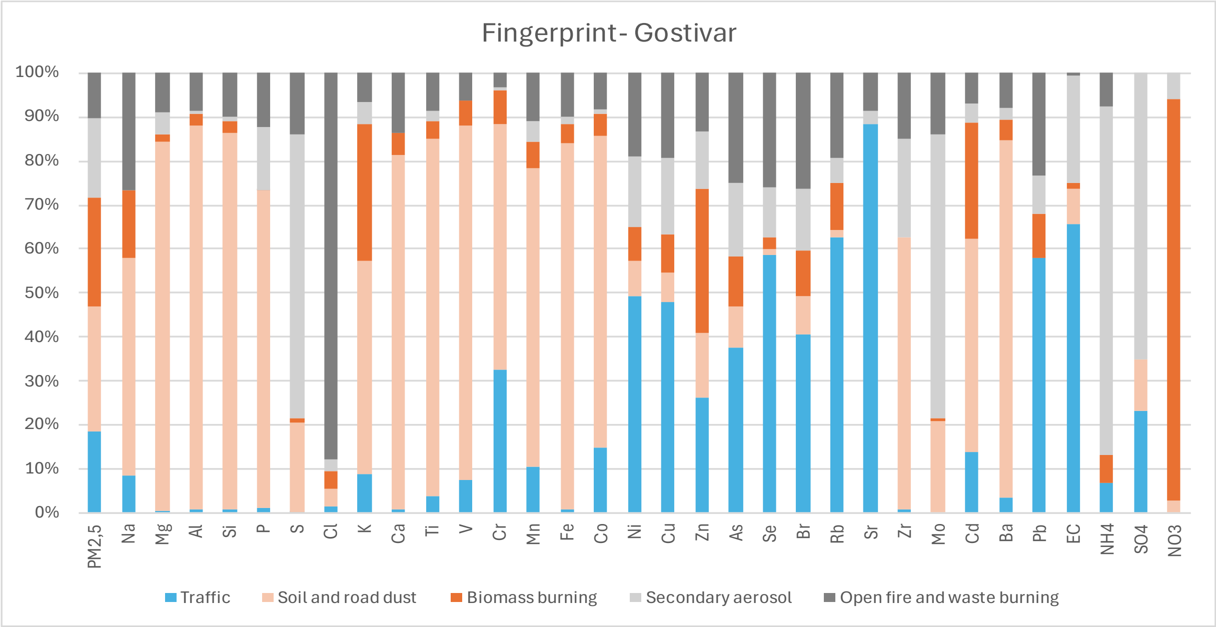


Figure 37. Factor fingerprint for Gostivar

Cl can be emitted from biomass burning and also from coal combustion, especially during the cold period [40]. It is also associated with biomass burning in PMF source profiles in Belgrade and Banja Luka [39]. In addition, NO_3^-, and NH_4^+ also contributed significantly to the biomass burning factor. Biomass burning is an important natural source of NH_3 [41] which rapidly reacts with HNO_3 to form NH_4NO_3 aerosols. The presence of NH_4NO_3 aerosols in biomass burning plumes, has also been reported previously [41, 42].

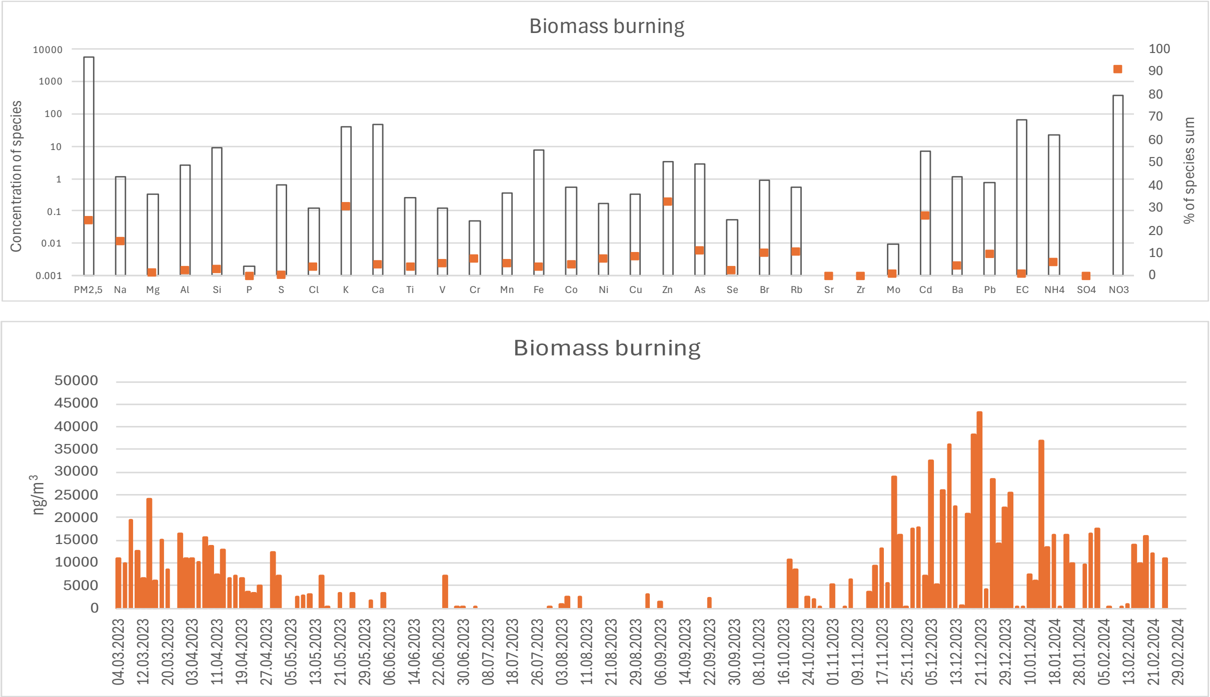


Figure 38. Biomass burning factor profiles in Gostivar

Evaluation of seasonal pattern of this factor clearly confirm attribution of this factors to biomass burning emissions that usually occur only during the cold months.

Traffic includes particles from several different sources including vehicles exhaust, mechanical abrasions of brakes and tires, road (resuspended) dust and road salting. All sources associated have their own specific fingerprints, and can be identified by 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.

The vehicle exhaust, including diesel and gasoline, consist high percentage of organic and elemental carbon, Fe, Pb, Zn, Al, Cu and sulphate. Similar species were also associated with traffic in PMF source profiles in most European and Central Asia urban areas [39].

Zn is a major additive to lubricant oil. Zn and Fe can also originate from tire abrasion, brake linings, lubricants and corrosion of vehicular parts and tailpipe emission [43-46]. As the use of Pb additives in gasoline has been banned, the observed Pb emissions may be associated with wear (tyre/brake) rather than fuel combustion [47].

Fe and Al is likely associated with vehicles part wear, such as tyre/brake wear and road abrasion, and are common species in case sampling sites are located close to major roads.

These results suggest the contribution of both exhaust and non-exhaust traffic emissions to several different factors that can be 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].

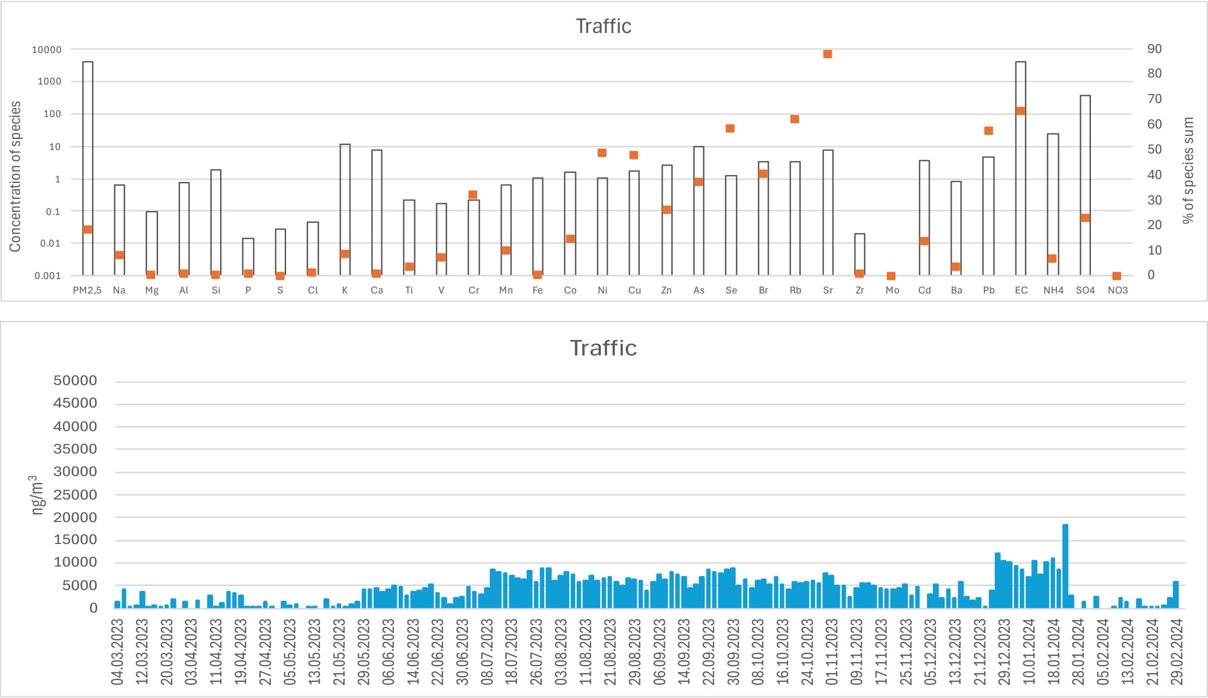


Figure 39. Traffic associated factors for Gostivar dataset

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. 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.

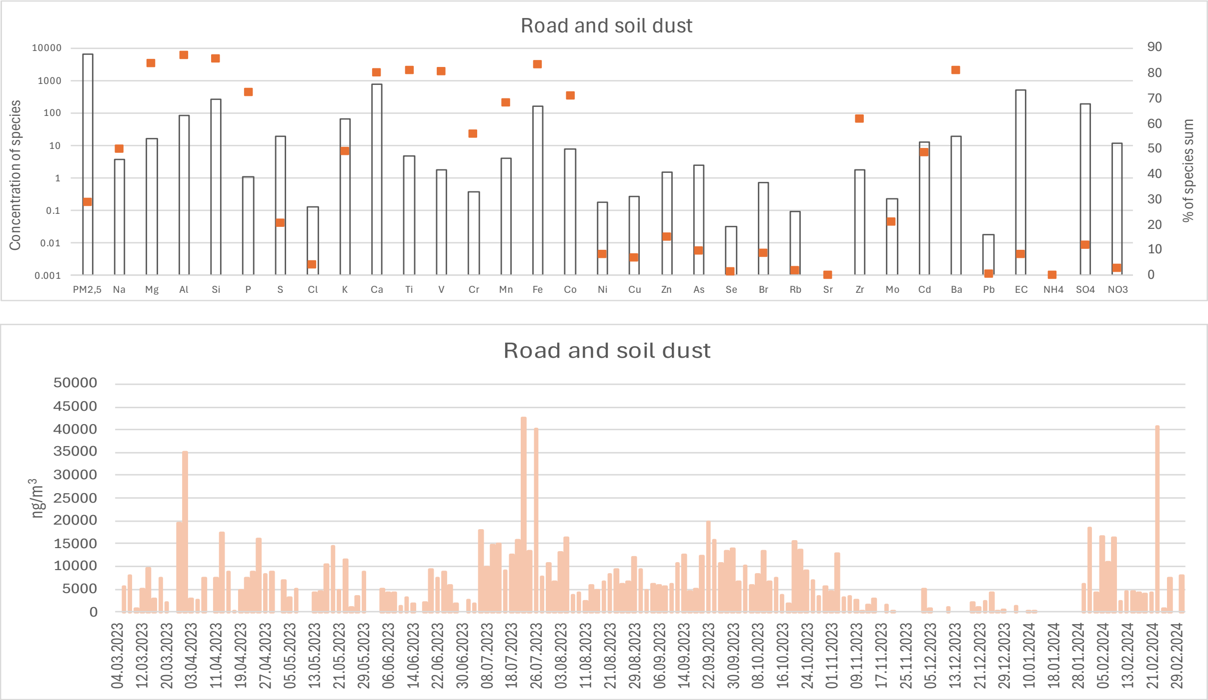


Figure 40. Mineral dust factor profiles

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.

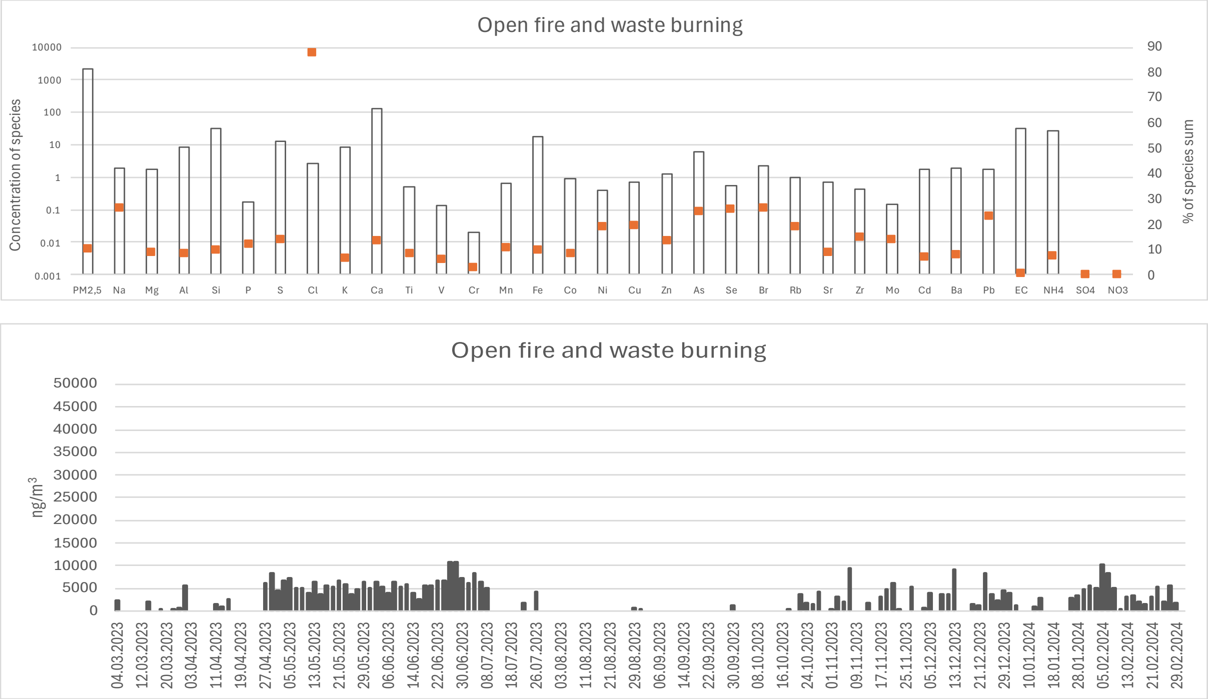


Figure 41. Open fire burning factor profile

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.

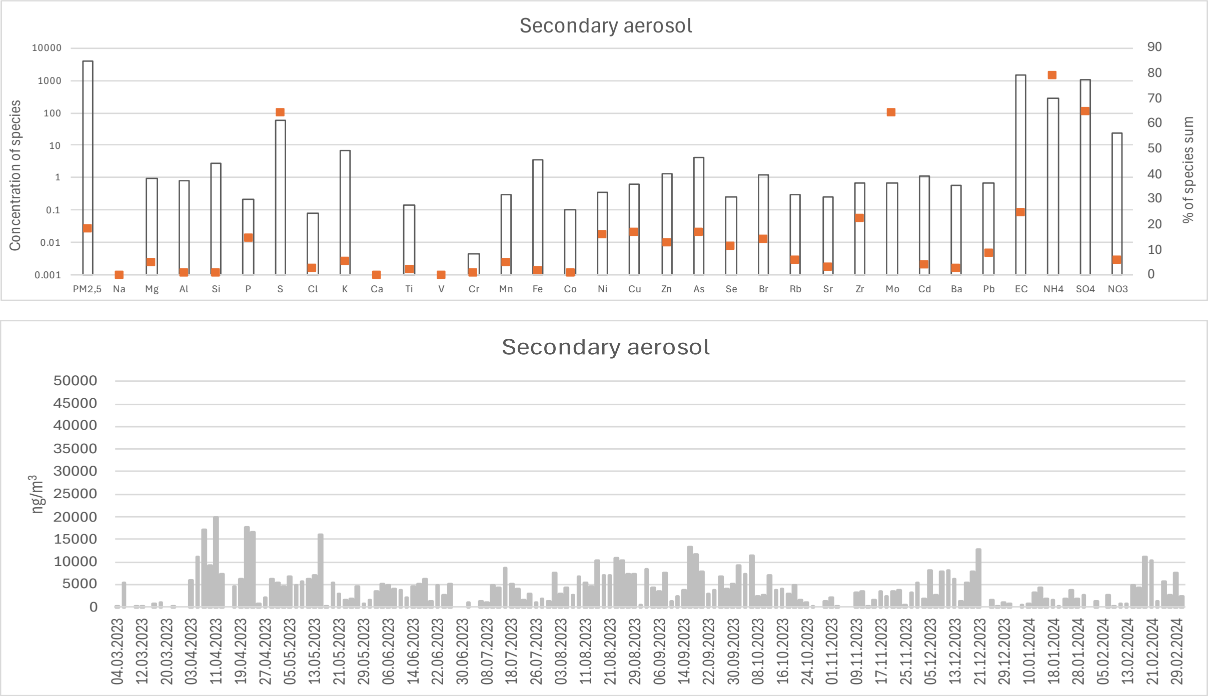


Figure 42. Secondary Aerosols factor profile

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 Gostivar include biomass burning, open fire and waste burning, traffic, secondary aerosols and road and soil dust.

The most dominant source of pollution in Gostivar is road and soil dust, also known as mineral dust, which consists of particulate matter primarily originating from construction activities and the resuspension of deposits on roadways. In this specific case, the urban area is surrounded by a large number of construction material quarries, which are also considered significant primary sources of mineral dust.

This source significantly contributes to the total particulate mass (PM2.5), with an increasing contribution during dry seasons, ranging from 0.6 to 15.2 µg/m^3. The monthly contributions from this source reach 57 %, while the annual relative contribution attains a notable 28 %.

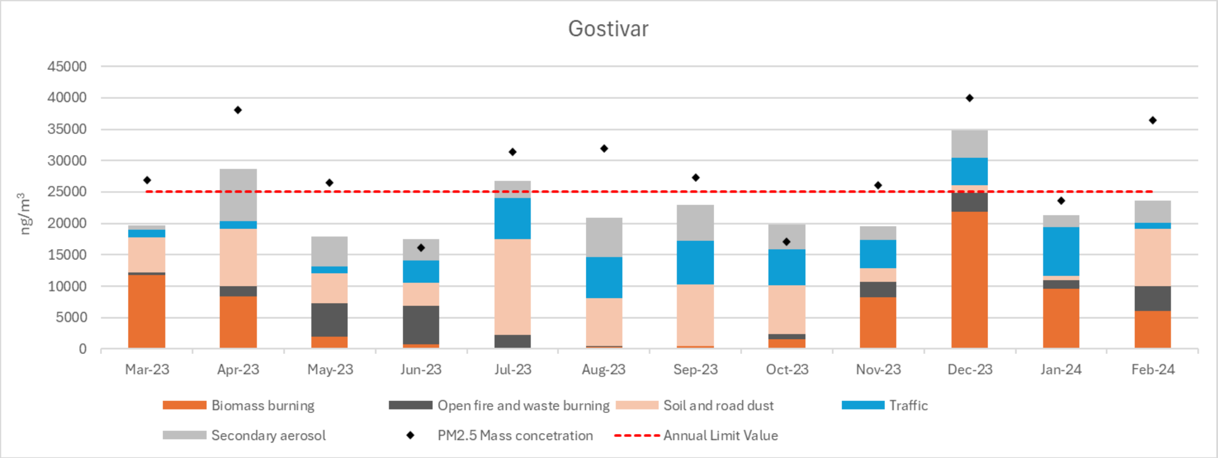


Figure 43. Average monthly contributions to total particulate mass (PM 2.5) – Gostivar

Biomass burning was also a significant source in the municipality of Gostivar 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 season ranged from 6 to 21.8 µg/m^3. The relative contributions (%) of biomass burning to total particle mass demonstrate significant seasonal variability, with this source accounting up to 62.7 % during winter months, and although entirely seasonal, biomass burning accounts for a significant annual relative contribution of 26 %.

Annually, traffic represents the third in rank air pollution source, demonstrating a steady contribution throughout the year, with a notable increase during the summer and fall months, ranging from 1 to 7.8 µg/m^3. The annual relative contribution of traffic constituted 18 % of the total particulate mass (PM 2.5), with monthly relative contributions varying between 4.4 % and 36.8 %. 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.

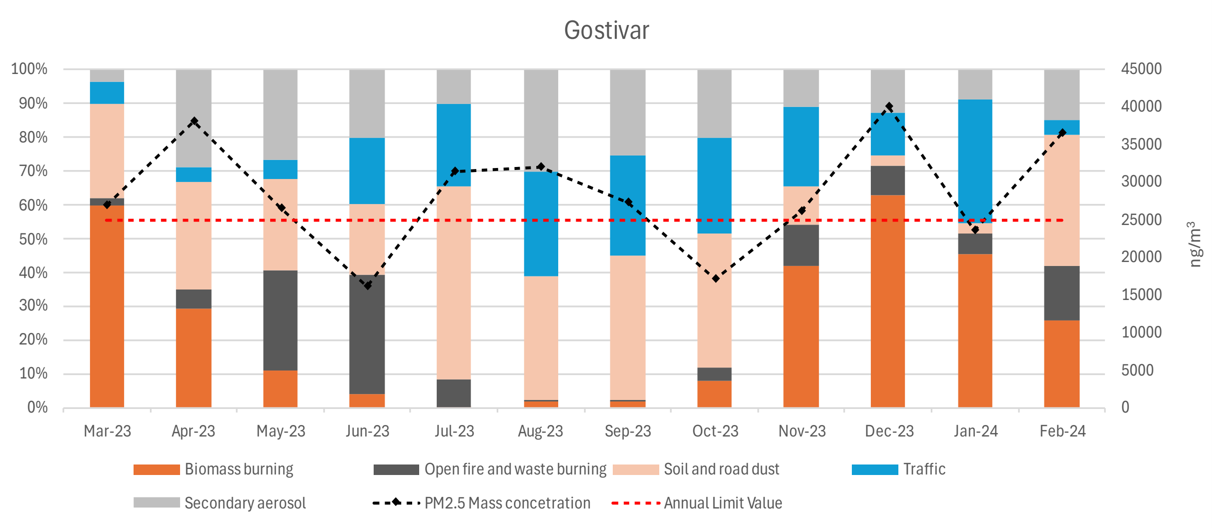


Figure 44. Relative monthly contribution – Gostivar

Open fires and waste burning include the combustion of crop residue, along with agricultural and garden waste materials, as well as landfill fires and wildfires. This category also covers the incineration of various waste materials in household stoves or small industrial boilers. We primarily observe this source in the spring and early summer, but we also note significant contributions in the autumn and winter periods. The monthly contribution from this source can reach up to 6.2 µg/m^3 or 35.3 %, while the annual contribution is 10 %.

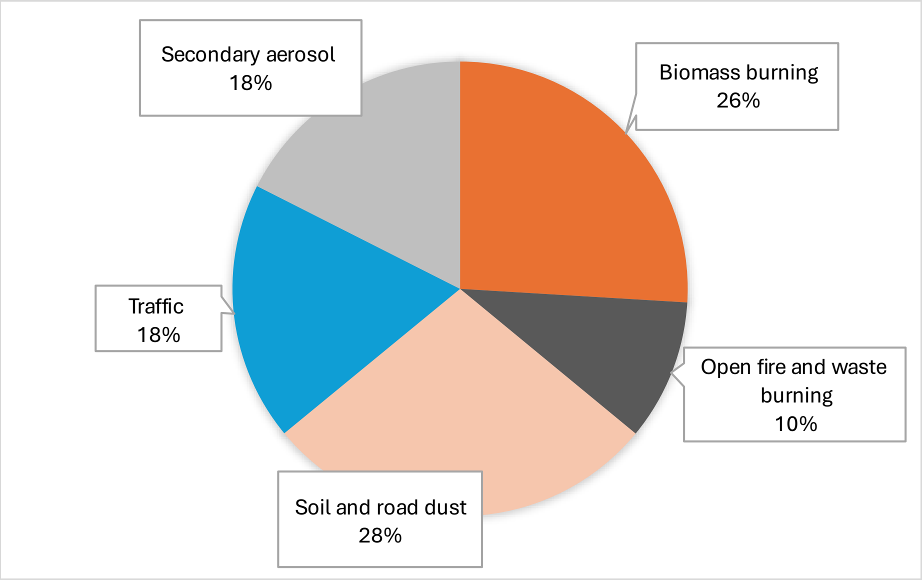


Figure 45. Relative annual contribution of PM 2.5 sources at Gostivar

Secondary aerosols are particles formed by chemical reactions in the atmosphere, influenced by sunlight, ozone, and humidity. Secondary aerosols have the biggest contribution during the coldest and hottest months, probably because there are more gas precursors in winter and chemical reactions from high temperatures in summer. The contribution of secondary aerosols ranges from 0.7 to 8.3 μg/m^3. The annual relative contribution of secondary aerosols was 18% of the total particle mass (PM2.5), with monthly contributions displaying significant variability, ranging from 3.6 % to 30.2 %.

6. Conclusions and recommendations

The urban region of Gostivar suffers poor air quality for an extended period of time. Particulate matter (PM 10) concentrations continuously exceed the set threshold limits. Between 2018 and 2021, Gostivar'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 Gostivar. The activities conducted were complied with the rigorous methodology outlined in the European handbook on air pollution source apportionment using receptor models (Revised edition 2019, JRC) and included a one-year ambient aerosol sampling and chemical speciation program, supporting the development of a multivariate receptor model.

The sampling program started on March 4, 2023, and until the end of March 2024, 191 samples were collected, with a 24-hour sample being taken every other day. The sampling process was conducted in strict accordance 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 utilized for elemental composition analysis, optical transmissiometry for quantifying elemental carbon content, and spectrophotometry for identifying water-soluble ions.

The daily average PM2.5 concentrations measured at the Gostivar monitoring site exhibit significant daily and seasonal variations, exceeding all national and European Union limits, targets, and thresholds for human health protection. Concentrations measured ranged from a minimum of 4.7 $\mu g/m^3$ to a maximum of 153.1 $\mu g/m^3$, resulting in an average annual value of 29.1 $\mu g/m^3$, which exceeds the annual threshold limit value of 25 $\mu g/m^3$ by 16%. The percentage of days surpassing the annual limit for PM 2.5 (25 $\mu g/m^3$) was an alarming 50% (87 out of 174 valid daily readings).

Modelled data, show that there is no apparent variation in particulate matter concentration by day of the week or time of day during the spring, summer, or even autumn. On the opposite side, although there are no significant differences between the days of the week, during the winter there are expressed daily variations with distinct peaks in particulate matter levels at specific times of the day (early morning and late evening). This pattern is often influenced by an interaction of meteorological factors, anthropogenic activities, and local emissions, and is predominantly attributed to the increased utilization of woodstoves and other solid fuel heating means, which discharge substantial quantities of particulate matter into the atmosphere.

Polar plots generated for the Gostivar area demonstrate concentration variations influenced from local meteorological conditions, notably indicating that elevated PM concentrations are exclusively observed during the winter season and are associated with the occurrence of weak winds (1 m/s) from all directions. Furthermore, non-parametric wind regression (NWR) plots also demonstrates that high concentrations are associated only with weak winds from all directions, which indicates that the pollution is local (from the immediate vicinity). Non-parametric regression defines the northwestern part of the urban zone and the village of Debreshe, the southwestern part of the city and the villages of Dolna and Gorna Banjica as the most significant directions.

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 Gostivar include biomass burning, open fire and waste burning, traffic, secondary aerosols, road and soil dust, and fuel and residual oil burning.

On annual level, mineral dust (road and soil dust), represents the primary air pollution source, demonstrating a steady contribution throughout the year, with a notable increase during the spring, summer and fall months. The annual relative contribution of mineral dust constituted 28% of the total particulate mass (PM 2.5), with monthly relative contributions reaching 57 %. Biomass burning is also one of the most important sources with relative contribution to total particulate mass accounting from up to 62.7 % during winter months, and although entirely seasonal, biomass burning accounts for a significant annual relative contribution of 26 %. The annual relative contribution of traffic and secondary aerosol is each 18 % of the total particulate mass (PM 2.5), and open fire and waste burning is 10 %.

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
Construction activities and aggregates production in queries, often involve extensive earthworks and during the dry season, can significantly impact local ambient air quality and raise average concentrations outside the heating season. Such activities can lead to increased annual averages and contribute to the violation of regulatory limits. Additionally, the resuspension of road dust is a crucial factor that may broaden the influence of local sources over a wider area.	Effective and cost-efficient methods for controlling fugitive dust are widely accessible. Usually, fugitive dust control programs at quarries or during construction works involve organizational and technical measures, ranging from regular supervision, fencing, tire washing, and simple water spraying up to sophisticated fog spraying systems that respond to dust generation intensity and wind changes. Mandatory fugitive dust management plans for all quarries and larger construction projects, along with effective implementation oversight, might substantially reduce ambient particulate matter concentrations, particularly outside the heating season. The UNDP's publication on solutions to air pollution (https://solutions.sdg-innovation-commons.org/en/view/pad?id=7168) and various technical reference documents cite notable examples.
Lesson No. 2	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. 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. 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. 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. 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.

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