Sweden
Sverige

UNDP

SOURCE APPORTIONMENT STUDY FOR STRUMICA 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”.

Document title:	Source Apportionment Study for Strumica urban area
Name of the organization:	University Goce Delcev, Stip, AMBICON Lab – Faculty of Natural and Technical Sciences
Country	Republic of North Macedonia
Project title:	Scaling-up actions to tackle air pollution
Project Number:	00122883
Submitted To:	UNDP, Skopje
Date of submission	03.04.2025
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

Contents

List of figures

List of tables

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.

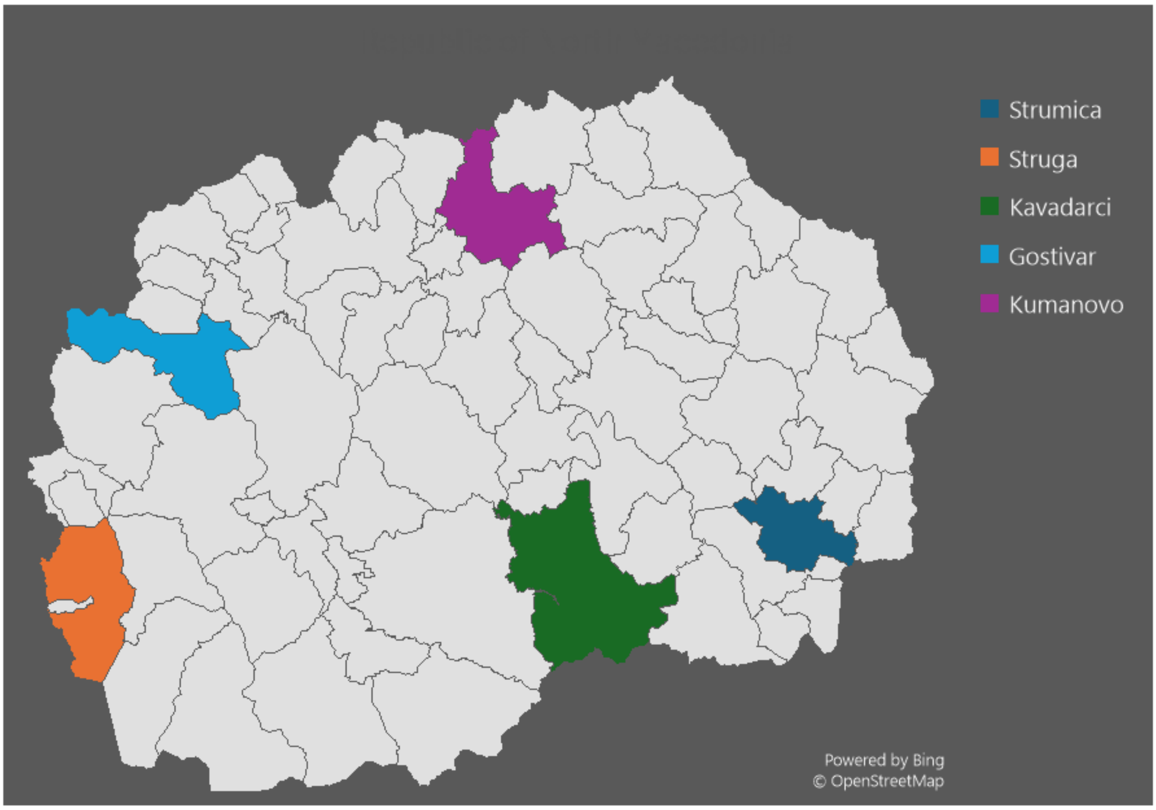


Figure 1. Map of municipalities included in this study

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. Strumica urban area

Strumica Municipality is located in the southeastern part of North Macedonia and belongs to the Southeastern Statistical Region. Covering an area of 321.89 km^2, the municipality is positioned in the Strumica Valley, which is surrounded by a range of mountains and has an average elevation of 239 meters above sea level. Skopje is 156 km away from Strumica Municipality, which is the largest and most prominent municipality in the Southeast region. It is located at the intersection of the borders with Bulgaria and Greece. The municipality comprises 25 settlements and shares borders with the Republic of Greece, along with five other municipalities: Bosilovo, Konce, Vasilevo, Novo Selo, and Valandovo (Fig. 2).

According to the 2021 Census, Strumica had a total population of 49 995, with 17 400 households and 24 621 apartments and houses.

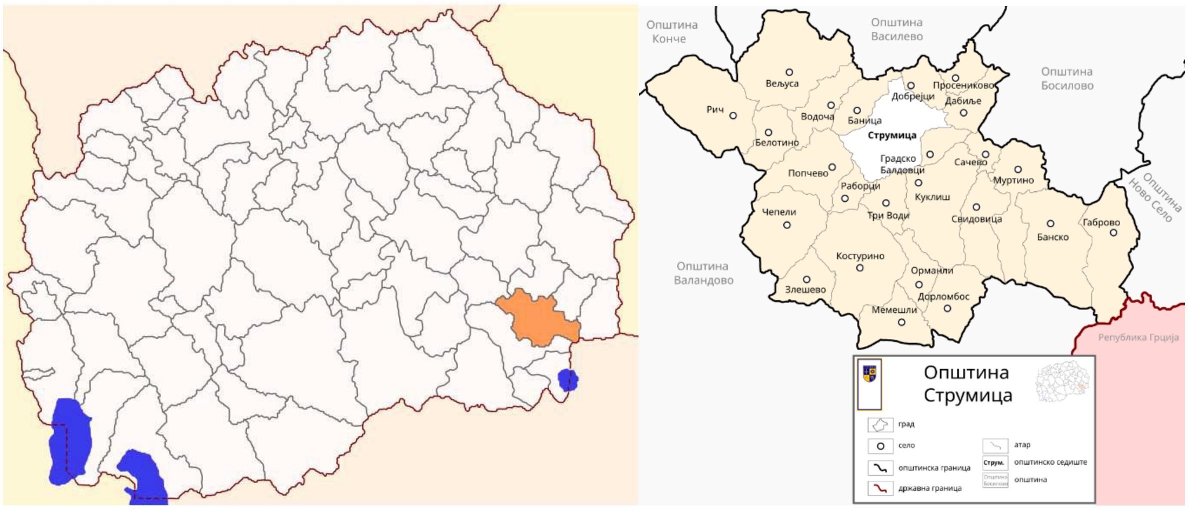


Figure 2. Location of Municipalities of Strumica

The Belasica Mountains to the southeast, Ograzden Mountain to the northeast, and Elenica Hills to the west encircle the Strumica Valley.

The Strumica River, featuring a 31-kilometer regulated riverbed, serves as the primary watercourse in the Strumica Valley. The Turija River and Monospitovo Canal, which includes the Vodochnica and Trkanja rivers, function as the left and right tributaries of the Strumica River, respectively.

The Strumica River Basin forms part of the larger transnational Struma River Basin [1].

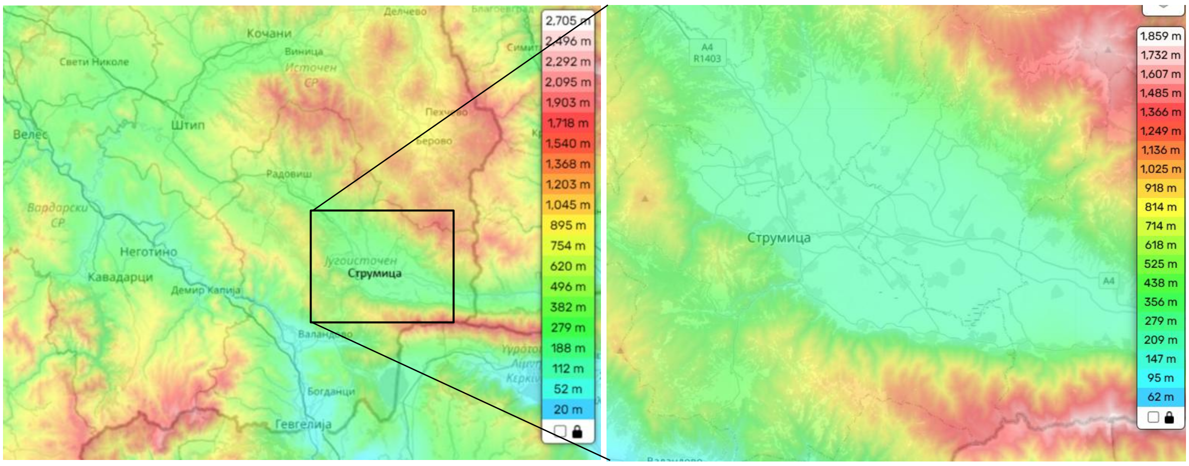


Figure 3. Strumica topography map [2]

2.2. Climate

The municipality of Strumica's unique geographic and topographic location is characterized by two zonal climates: sub-Mediterranean and East-Continental. These climates converge to create a distinctive feature of the area: long, warm summers with high average daily temperatures and minimal precipitation, alongside cold winters with winds originating from various directions. The average annual air temperature is 12.6 °C, with the highest average monthly temperatures occurring in July (23.7 °C) and the lowest in January (1.0 °C). The temperature amplitude is 22.2 °C, while the difference between the absolute maximum of 40.5 °C and the absolute minimum temperature of -24.06 °C is 64.5 °C [1].

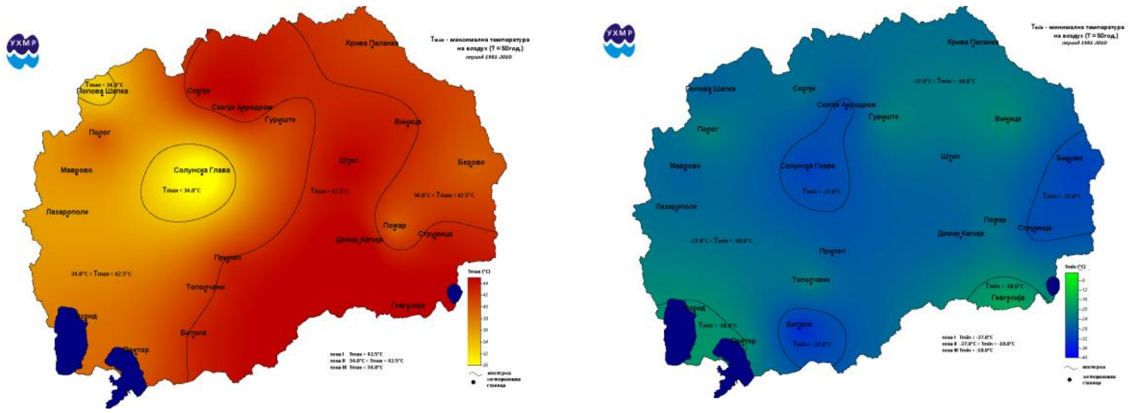


Figure 4. Maximum and minimum temperature maps for North Macedonia with probability of occurrence of 0,002% (Source: Climate maps, UHMR, 2020)

The Strumica region stands out due to its extended duration of sunny days and elevated light intensity, which favourably influences fruiting. There are approximately 230 sunny days and an average of 2,377 hours of sunshine annually. Typically, there are about 20 days of fog during November, December, and January.

The climatic conditions in the Strumica region are characterized by reduced annual precipitation, increased aridity, and a variable pluviometric regime, influenced by sub-Mediterranean factors from the Aegean Sea and continental climate, along with lower winter temperatures. However, long-term droughts (lasting more than a month) are uncommon in Strumica, where the annual precipitation averages 547.2 mm, peaking in the fall and spring (April–May) [1].

On average, there are 160 frost days (December-January) and 18 recorded days of snowfall [1,3].

The predominant winds in the region are northwestern and southwestern, occurring over 10 % of the time, with velocities ranging from 0 to 4 m/s, and infrequently reaching speeds of 4 to 6 m/s. North winds manifest over 10 % of the time across all seasons, albeit at reduced velocities (0 to 2 m/s), with infrequent instances of higher speeds during the winter season. South winds occur throughout all seasons for 5 to 10 % of the time, with infrequent instances of higher velocities (up to 6 m/s). It is noteworthy that all other wind directions exhibit frequencies of approximately 5 % throughout the year, but at lower speeds. Calm conditions occur most frequently in autumn, accounting for 13 % of the time, and in summer, comprising 6.8 % of the time.

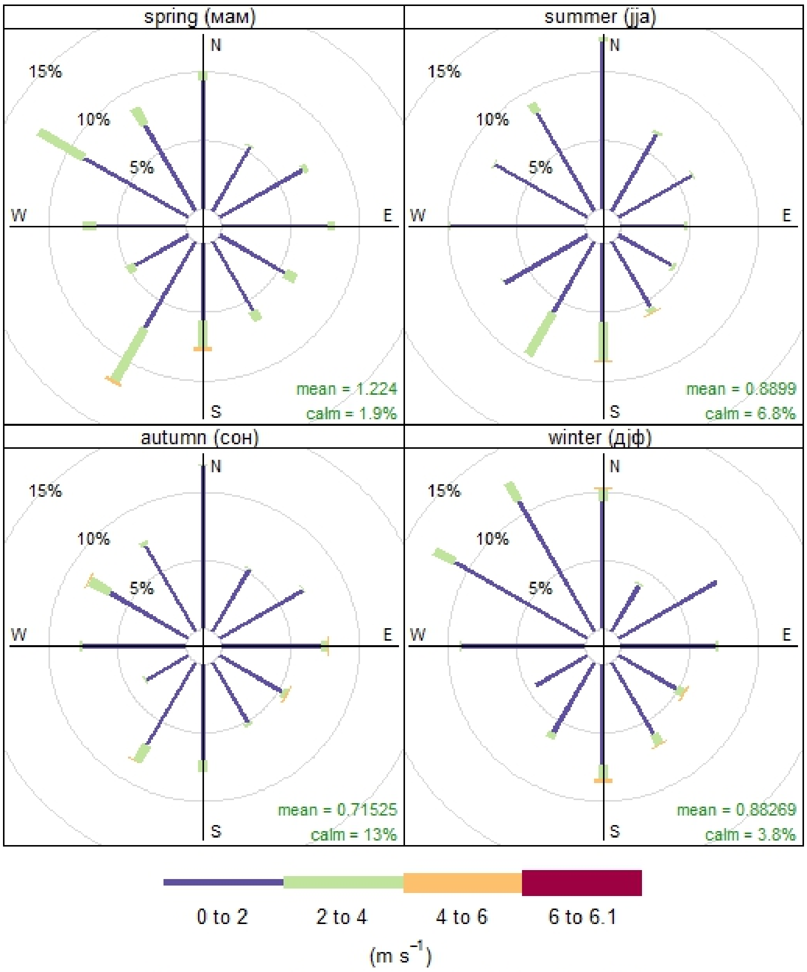


Figure 5. Seasonal wind roses during the monitoring period (March 2023 to February 2024, AMBICON Lab).

2.3. Transportation and energy infrastructure

The Municipality of Strumica is situated directly beneath the tripoint of our country's international borders with the Republic of Bulgaria and the Republic of Greece. The municipality's transportation connectivity to the Republic of Bulgaria via the Novo Selo border crossing and the international route in the Vardar River Valley is of significant importance. The A4 highway traverses the Municipality of Strumica, linking the border with the Republic of Bulgaria (Novo Selo border crossing) to Radovish, Stip, Sveti Nikole, Miladonovci, Pertovec, and Skopje and extending to the Republic of Kosovo at the Blace–Stenkovec border crossing. Additionally, the Municipality of Strumica has indirect access to the A1 highway via the regional road R1401 and to the A3 highway through the regional road R1302.

Strumica has one bus station that facilitates local, intermunicipal, and international passenger transport. In September 2024, Strumica inaugurated public transportation for the first time, featuring ten electric buses. There is a proposal for the development of a bus base, which would include photovoltaic collectors mounted on 5,000 square meters of roofing to meet the charging requirements of the electric buses [6]. The Makstat database indicates that the quantity of road motor vehicles and trailers in the Municipality of Strumica has remained relatively consistent over the past three years, with notable growth only in the number of passenger cars. Figure 6 presents comprehensive data on vehicle numbers.

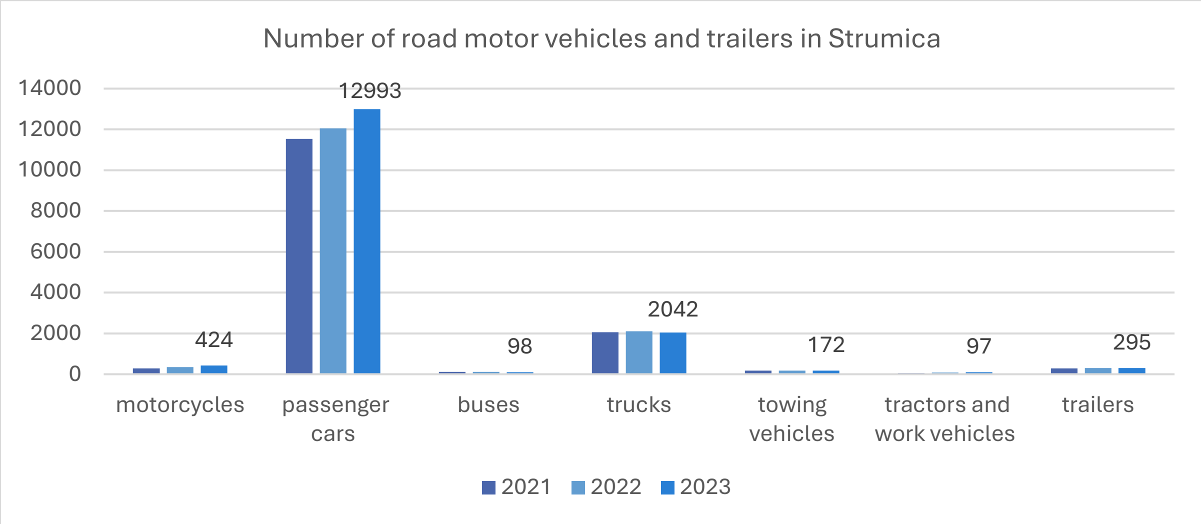


Figure 6. Number of road motor vehicles and trailers in Strumica [5]

The largest share of electric energy in the region is provided by a national power network managed by EVN Macedonia-KEC Strumica, while production from small photovoltaic plants remains minimal. The electricity network spans a total of 892 kilometers, with 103 kilometers linked by cable. All settlements are served by two 110/10 kV substations and 240 10/04 kV substations, with 145 owned by the network operator (EVN) and the remaining 95 owned by individual or group consumers [1].

Since 2011, the urban area of Strumica has been connected to a virtual gas distribution network that currently extends 20 kilometers, with plans to expand it to 50 kilometers. Since then, most public buildings have been connected to the network and use natural gas as an energy source for heating. This includes all schools and kindergartens, as well as most municipal administrative buildings in Strumica, emphasizing that gas and electricity serve as the primary energy sources for public buildings, while wood and fuel oil play a minimal role (see figure 7). Although the municipality of Strumica offers financial support for households to connect to the gas network, the number of individual consumers remains negligible [4].

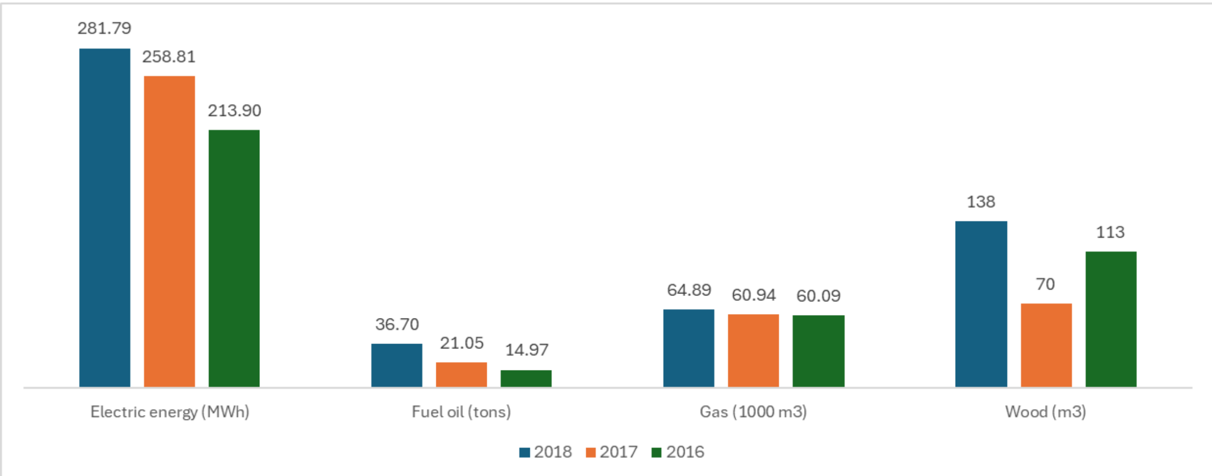


Figure 7. Consumption of energy in public buildings in the municipality of Strumica from 2016 to 2018 [4]

2.4. Industry and service providers

The main economic sectors in the Municipality of Strumica are agriculture and animal husbandry, followed by the food industry, the wood industry, and the mineral and metal processing and textile industry (heavy and light clothing). The most prevalent economic sector (39.1% of active business entities in 2020) in the municipality is wholesale and retail trade. In second place is the processing industry, representing 10.8 %, and in third place are professional, scientific, and technical activities (10.7 %). Agriculture, forestry, and fishing account for 2.7 % of active business entities, mining and quarrying 0.3 %, construction 5.1 %, and transport and storage 5 %. This region is also recognized nationally as one of the largest producers of vegetables in controlled environment spaces, which includes several thousand hectares of covered area. However, excluding larger producers covered by IPPC permits, there is no official data regarding heating systems and types of fuel used.

The processing industry primarily encompasses establishments for processing primary agricultural goods. This sector includes the manufacturing of canned vegetables, dairy processing, meat processing, and the processing and fermentation of tobacco. Additionally, it includes the milling and baking industry, as well as small-scale production facilities focused on confectionery. Other processing industries consist of plants for furniture manufacturing, metal fabrication, concrete prefabrication, quarrying, mineral processing, and the production of construction materials.

The Register of A IPPC Permits indicates that the Ministry of Environment and Spatial Planning has granted four (4) A IPPC permits within the municipality of Strumica for the following companies:

- Ograzden AD – Strumica (automated mill and facility for the grinding and packaging of feldspar),
- AD Industry for Building Materials Elenica – Strumica (brickworks),
- Sim Engineering DOO/Universal Gradba DOOEL - Strumica (asphalt production plant);
- BUL-BUILDING DOO, Strumica (cultivation of spicy, aromatic, and medicinal plants for pharmaceutical use).

Elenica Brickworks A permit has expired, and new permit is not officially published.

The majority of plants indicate that gas and electricity are the principal power sources, with small amounts of fuel oil used for heating purposes. Ogražden AD Strumica utilizes methane gas (LNG) as a fuel source for thermal energy generation in a drying process. Sim Engineering and Universal Construction asphalt production plant primarily utilize electricity and consume only low amounts of fuel oil, with an annual consumption reported at 19 tons. BUL-BUILDING DOO located in Strumica also utilizes electricity and a minimal quantity of fuel oil for its heating boiler, with an average yearly use of 5 tons. It is important to note that since the permit for Elenica Brickworks has expired, no official data regarding the energy sources and fuel types utilized is available; however, prior publicly accessible data suggests an annual consumption of approximately 1 500 tons of pet coke for the brick kiln.

The National Register of B-IPPC Permits indicates that the Municipality of Strumica has issued a total of twelve (12) B-IPPC permits, with only six companies currently active;

- AGROPROIZVOD ZZ – Strumica, SKRKA Quarry Rich-Belotino (limestone quarry with crushing and classification plant),
- AD "GROZD" – Strumica (factory for alcoholic and non-alcoholic beverages),
- Kipo DOOEL - Strumica (limestone quarry for crushing and classification plant),
- PORTLAND-OPC DOOEL - Strumica (Pre-Mixed Concrete Plant),

- SILOTER – DOO, Vodocha - Strumica (Pre-Mixed Concrete and concrete products plant);
- DG "BETON-PM" - Strumica (Pre-Mixed Concrete and concrete products plant).

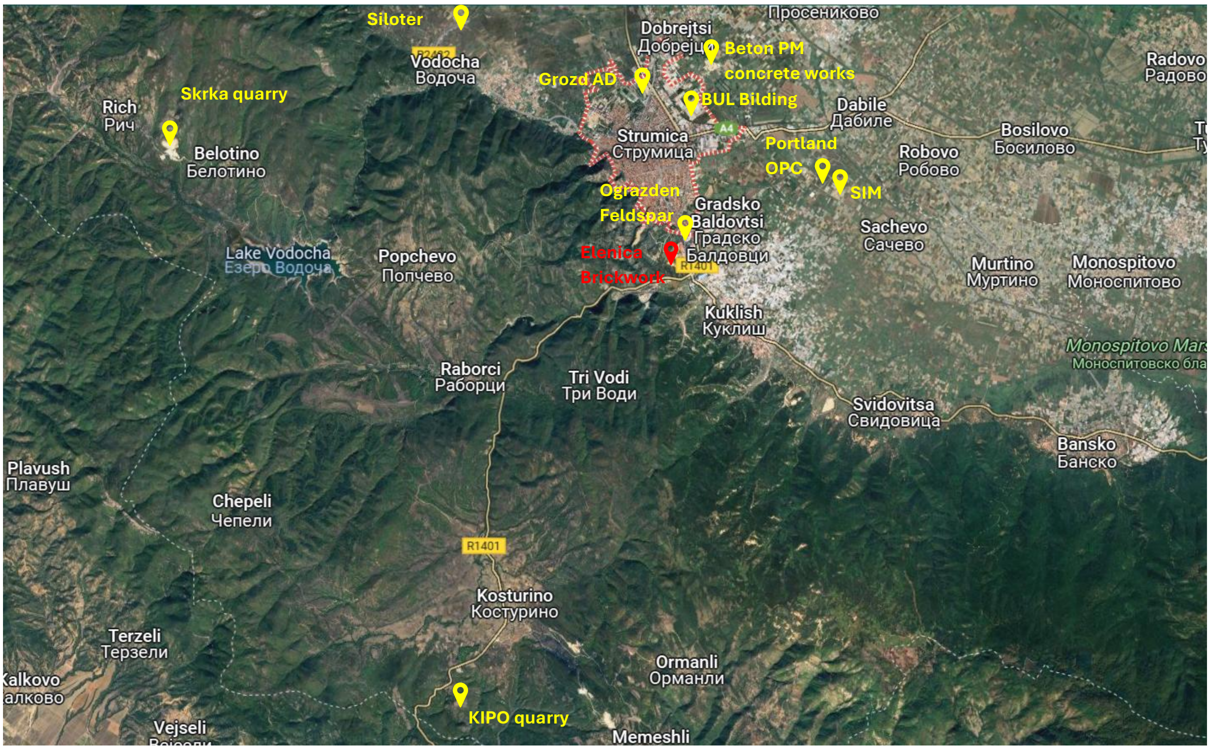


Figure 8. Location of IPPC installations in Strumica Municipality under A and B licenses.

These installations also indicate that electricity serves as a primary power source. This list includes limestone quarries and concrete mixing plants, which utilize electricity to carry out the technological processes. The "GROZD" Strumica beverage factory, specializing in the production and sale of both alcoholic and non-alcoholic beverages, has reported an annual consumption of approximately 90 tons of fuel oil for heat production, in addition to its electricity usage. No consumption of coal or other solid fuels has been reported.

As mentioned earlier, most public buildings and institutions, such as schools, kindergartens, hospitals, and administrative services, primarily rely on gas boilers for heating, using only small amounts of oil and solid fuels.

2.5. Historical data on ambient air quality

The most recent air quality assessment in Strumica municipality was performed during the development of the 2024 Air Quality Improvement Plan, utilizing data from the state monitoring network covering the period from 2019 to 2023. 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 Strumica 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.

The average annual values of NO_2 during the assessment period ranged from 8.16 to 18.40 μg/m^3, which is well below the stipulated annual limit value of 40 μg/m^3. Furthermore, within the specified timeframe, the hourly limit values established for the protection of human health (set at 200 μg/m^3) were not exceeded at any point.

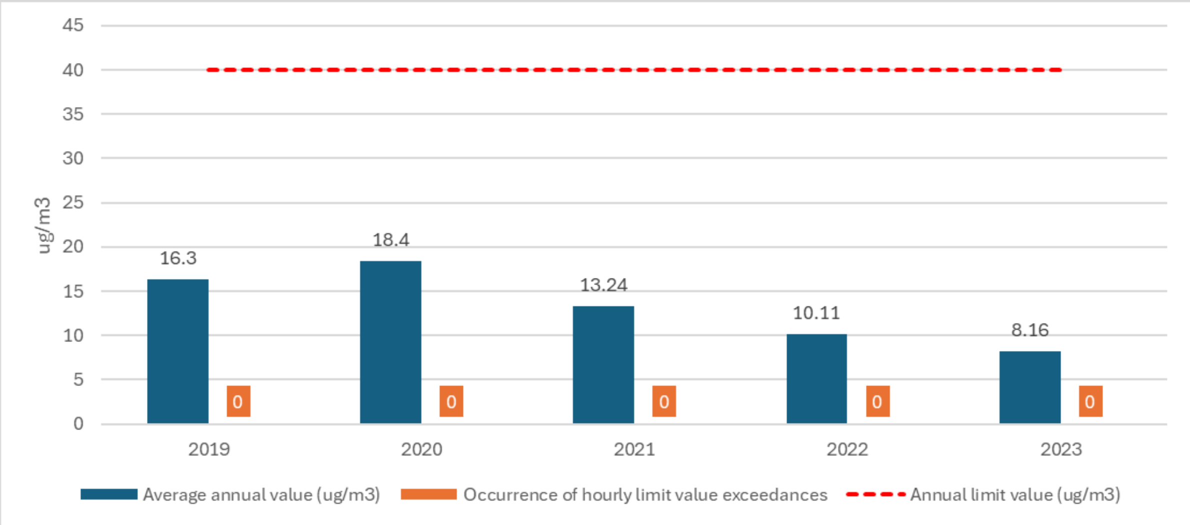


Figure 9. Average annual concentrations of NO_2 from 2019 to 2023 [1]

Similarly, carbon monoxide (CO) is classified as non-critical because there were no instances of exceeding the health protection limit value of 10 mg/m^3 during the specified time period.

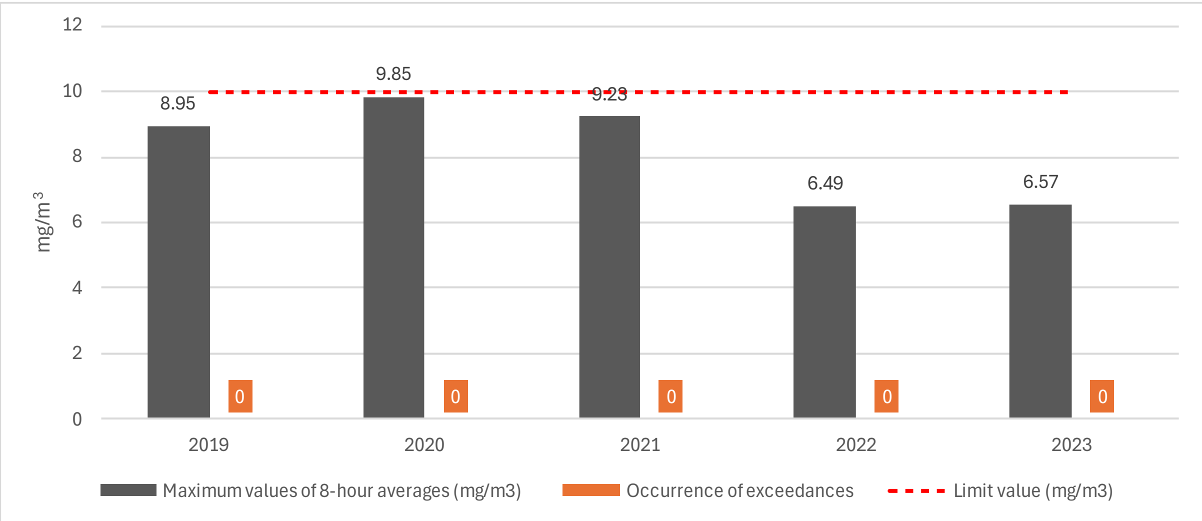


Figure 10. Maximum 8-hour averages of CO from 2019 to 2023 [1]

Annual SO_2 concentrations from 2019 to 2023 ranged between 1.82 and 4.31 µg/m^3, remaining well below the regulatory limit of 20 µg/m^3 established for ecosystem protection. During the same period, average daily values peaked at 15.88 µg/m3, while hourly values reached 57.83 µg/m^3, with elevated levels occurring solely in the cold season and during significant pollution events.

Although there were no exceedances of the specified daily and hourly limit values, and maximum values remained far below the thresholds of 125 µg/m^3 for daily averages, and 350 µg/m^3 for hourly averages, the most extreme values recorded in Strumica are among the highest at the national level.

Since no exceedances of the limit values were observed, indicating no direct concerns for human health or environmental conservation, no further assessments were performed.

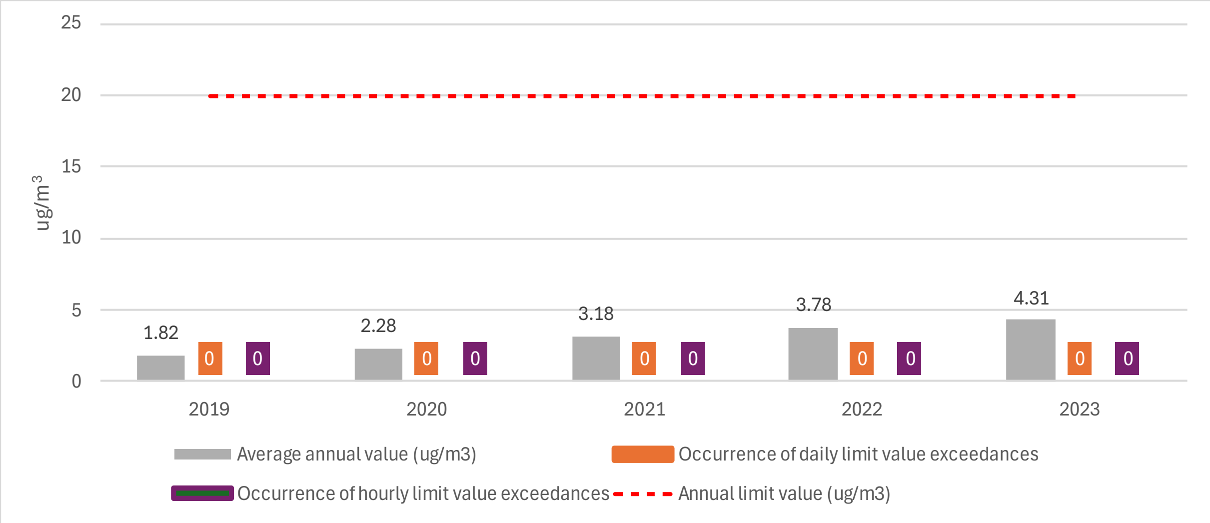


Figure 11. Average annual concentration of SO_2 from 2019 to 2023 [1]

However, considering public interests, we have also assessed the SO_2 concentrations during our monitoring campaign, which began in March 2023 and concluded in March 2024. We compared the data against limit levels and other monitoring sites, including Karpos – Skopje as an urban background site and Novo Lisice – Skopje as a site exposed to traffic and industrial emissions.

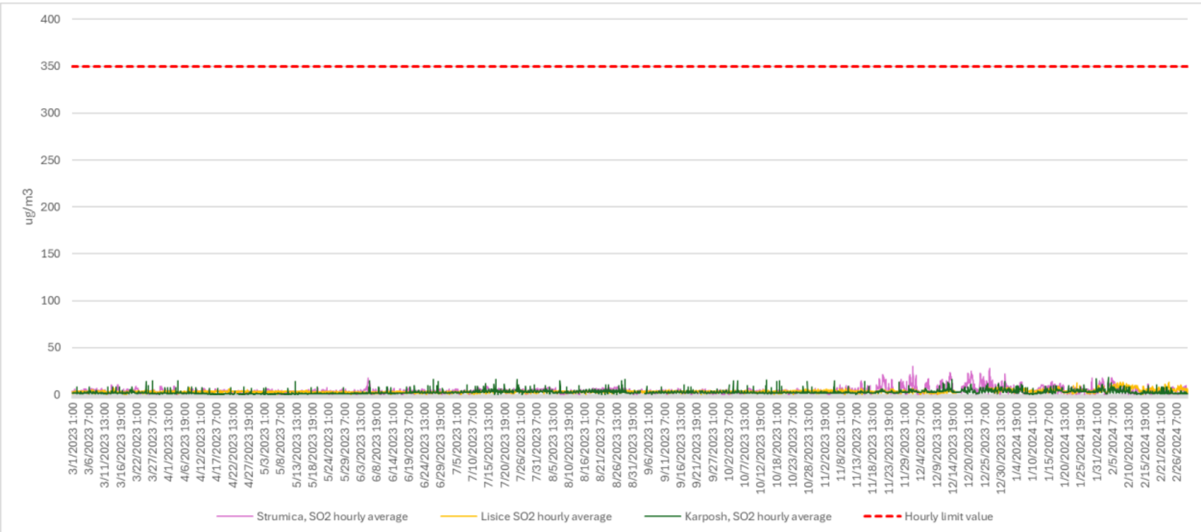


Figure 12. Hourly average concentrations of SO2 at Strumica, Karpos-Skopje, and Novo Lisice – Skopje during the monitoring campaign from March 2023 to March 2024

At all locations and especially in Strumica, elevated levels of SO_2 are particularly evident in late autumn and winter. The peak hourly average was recorded in Strumica at 30.32 μg/m^3, followed with Karpos at 18.25 μg/m^3 and Novo Lisice at 13.3 μg/m^3, but as illustrated in the chart above (Fig. 11), all values remained significantly below the hourly limit established for human health protection (350 μg/m^3).

The highest daily values recorded exhibit a similar pattern, beginning with 15.72 μg/m^3 in Strumica, followed by 10.71 μg/m^3 in Novo Lisice and concluding with 6.58 μg/m^3 at Karpos background site. All measurements remain significantly below the limit value of 125 μg/m^3 (see Fig. 12).

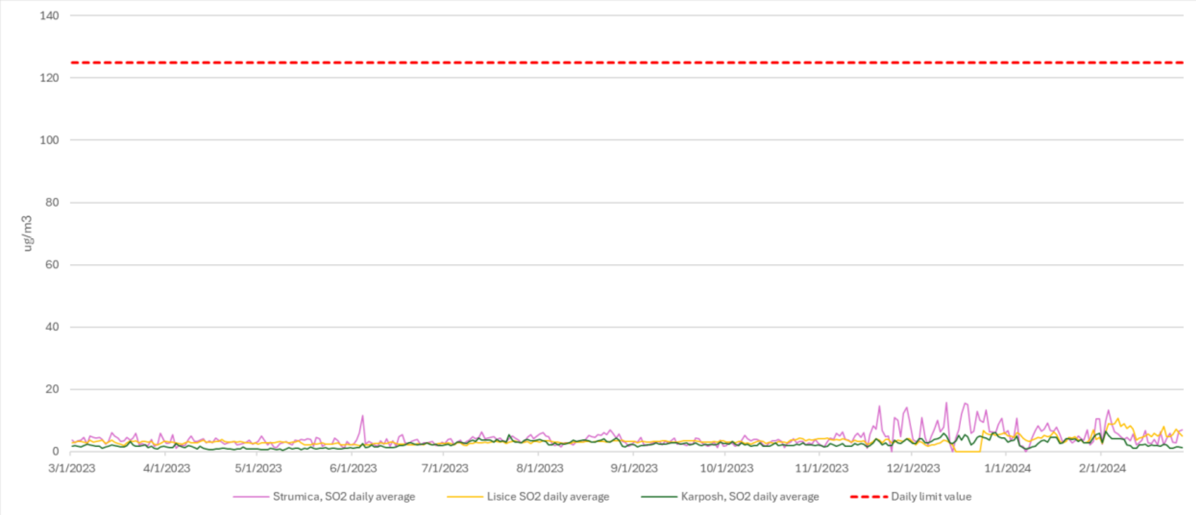


Figure 13. Daily average concentrations of SO_2 at Strumica, Karpos-Skopje, and Novo Lisice – Skopje during the monitoring campaign from March 2023 to March 2024

Annual average values also demonstrate an identical lineup, starting at 4.32 µg/m^3 in Strumica, 3.45 µg/m^3 in Novo Lisice, and 2.43 µg/m^3, all far below the annual threshold set for ecosystems protection of 20 µg/m^3. This situation is consistent with data from the past five years, as documented in the Strumica Air Quality Improvement Plan [1], and the classification of this pollutant as non-critical is considered valid.

While the combustion of fossil fuels, notably coal, pet coke, and oil, in power plants and industrial facilities is regarded as a primary anthropogenic source of SO_2, burning of biomass, particularly agricultural waste, is also acknowledged as a substantial contributor to atmospheric SO_2 emissions, potentially accounting for 80 to 90 % of total emissions in certain regions [7]. The combustion of biomass can significantly elevate SO_2 levels in the atmosphere, especially in areas characterized by intensive agriculture and the utilization of agricultural waste as fuel [8, 7]. Agricultural residues, including leaf's, straws and other plant debris, generally have a higher sulphur content compared to wood, and in combination with increased application of sulphur-containing fertilizers, likely contribute to the observed greater emissions [7, 9]. Thus, it is more plausible that increased SO_2 concentrations correlate with a significant quantity of agricultural waste (as well as other waste, such as scrap tires), utilized as heating fuel or burned in open fires, rather than being linked to industrial sources.

Ozone (O3) is the only gaseous pollutant that exceeded the limit levels for human health protection during the assessment period. The ozone data indicate that the human health protection threshold of 120 µg/m^3 was exceeded in 2019 and 2021, with no data available for 2020 and 2023.

The highest recorded ozone levels (hourly averages) occurred at 17:00 on 29 August 2019 (158.1 µg/m^3) and at 16:00 on 15 July 2021 (139.6 µg/m^3), with maximum 8-hour averages exceeding the limit documented in 2019 (143.52 µg/m^3) and in 2021 (129.2 µg/m^3).

The detected exceedances have a very brief duration and were not markedly elevated, therefore never reaching warning or information thresholds.

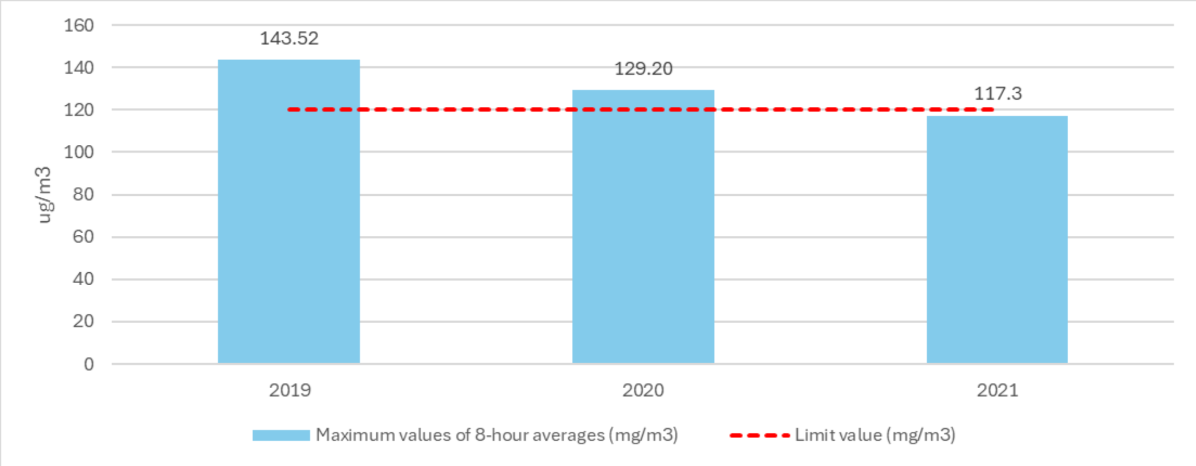


Figure 14. Maximum 8-hour averages of O_3 from 2019 to 2023 (μg/m³) [1]

Unlike gaseous pollutants, the measured concentrations of particulate matter consistently surpass all defined threshold values throughout the assessment period, especially during the colder seasons when prolonged episodes of severe pollution frequently occur.

The coarse particulate fraction PM10 consistently exceed the 24-hour limit value (50 μg/m³) and the annual limit value (40 μg/m³) from 2019 to 2023, excluding 2020 when sufficient data were unavailable. The total number of 24-hour limit exceedances throughout a calendar year ranges from 80 to 133, substantially exceeding the suggested threshold of 35 days. Average yearly concentrations surpass the annual limit each year, beginning with 21% above the limit in 2021, 32 % above in 2019, and reaching 33 % above the limit in both 2022 and 2023.

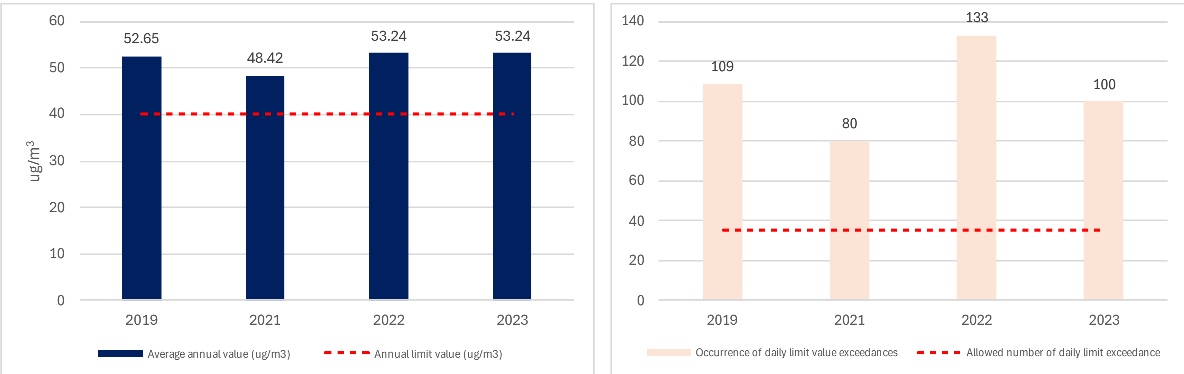


Figure 15. Average annual PM10 concentrations and number of exceedances of the 24-hour limit value in Strumica from 2019 to 2023 [1]

High concentrations are typically observed throughout the colder seasons, with daily averages reaching a staggering 424.7 μg/m³ on December 27, 2021, with daily averages exceeding 100 μg/m³ being common in late autumn and winter.

The fine particulate fraction (PM 2.5) has been observed since mid-2021, however sufficient information for yearly average assessment are available only for 2022 and 2023. The annual average concentrations for both, surpass the recommended limit value by 25 % in 2022 and 27% in 2023.

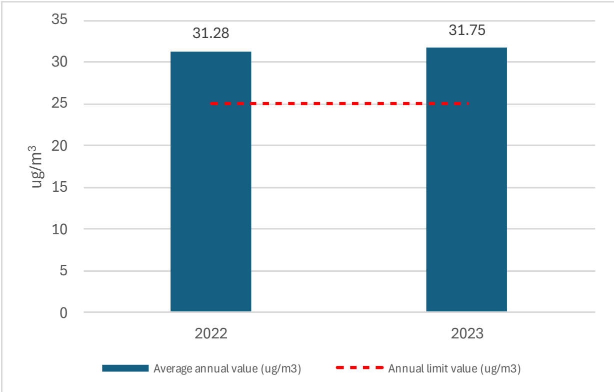


Figure 16. Average annual PM 2.5 concentrations in Strumica from 2021 to 2023 [1]

3. Major emission sources

Emission data and corresponding source profiles were compiled using several relevant sources, including the Air quality improvement plan for Municipality of Strumica [1], as well as the SPECIEUROPE repository [10], which contains chemical profiles of particulate matter obtained from source measurements conducted across Europe.

3.1. Emissions inventory

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

Calculations conducted follow recommended procedures based on the:

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

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

Emissions = Activity Data x Emission Factor

where:

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

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

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

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

	Pollutants (t/year)							
	CO	NH_3	NMVOC	NO_X	SO_X	PM10	PM2.5	TSP
Industry	0,14	0,00	116,76	0,84	0,07	41,32	4,16	136,43
Traffic	262,90	3,11	51,89	224,22	0,03	0,00	14,46	0,00
Public facilities	98,73	0,00	51,96	16,82	2,09	28,17	27,65	29,38
Households	970,95	16,95	145,50	12,60	3,86	184,21	179,36	193,94
Agriculture	0,00	41,32	24,31	6,18	0,00	1,37	0,72	3,04
Waste management	11,36	0,00	36,43	0,65	0,02	0,92	0,85	0,95
Natural sources	241,24	1,61	24,12	8,04	1,61	0,00	0,00	0,00
TOTAL	1585,32	62,99	450,96	269,36	7,68	255,98	227,20	363,75

Household heating is the primary contributor to particulate matter emissions, accounting for 79 % of PM2.5 and approximately 72 % of PM10 emissions. This is followed by emissions from industrial processes (16 %) and public buildings heating systems (11 %) in the case of PM 10. Public heating, which accounts for 12 %, and traffic, which accounts for 6 %, also significantly contribute to total PM 2.5 emissions.

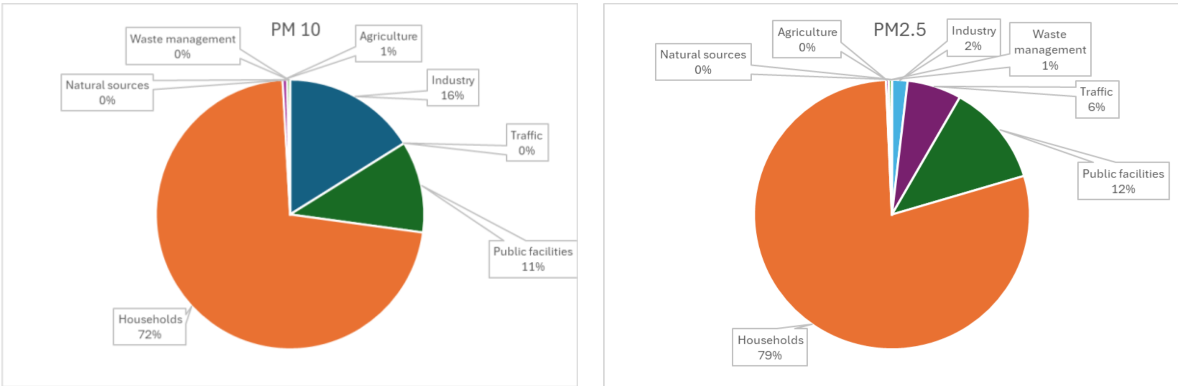


Figure 17. Sectoral contribution to particulate mater emissions [1]

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.

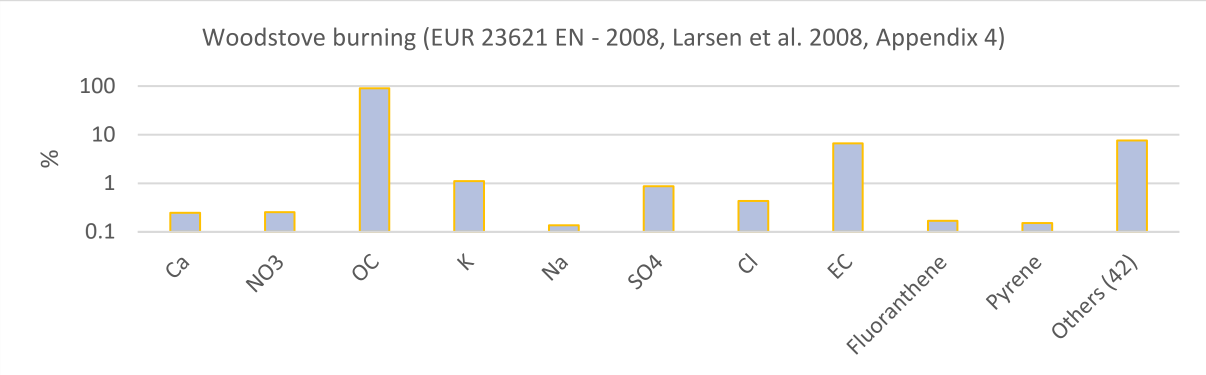


Figure 18. Woodstove burning chemical profile (closed fireplace)

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.

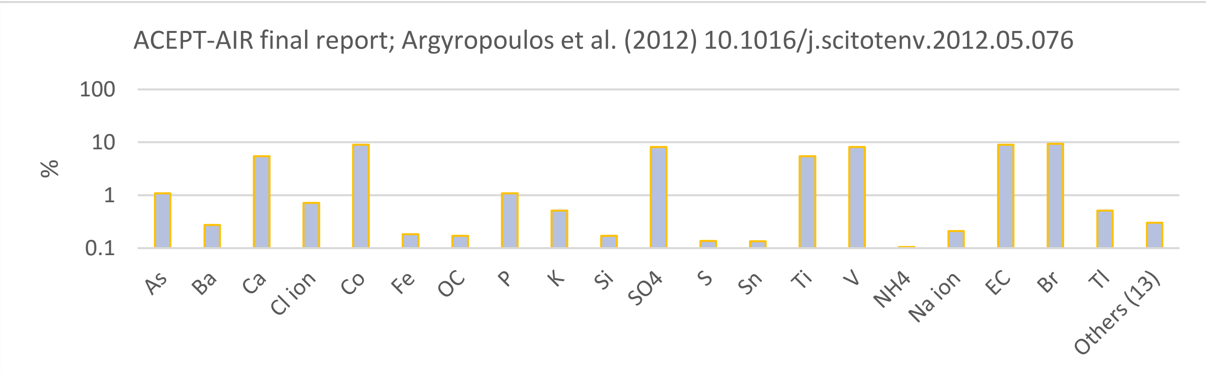


Figure 19. Open burning of crop residues chemical profile

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.

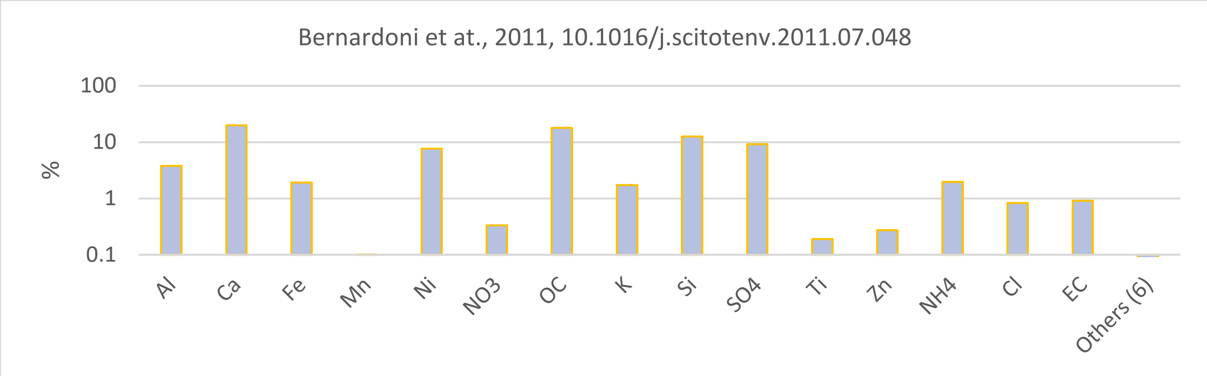


Figure 20. Construction activities chemical profile

Traffic source profile includes 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.

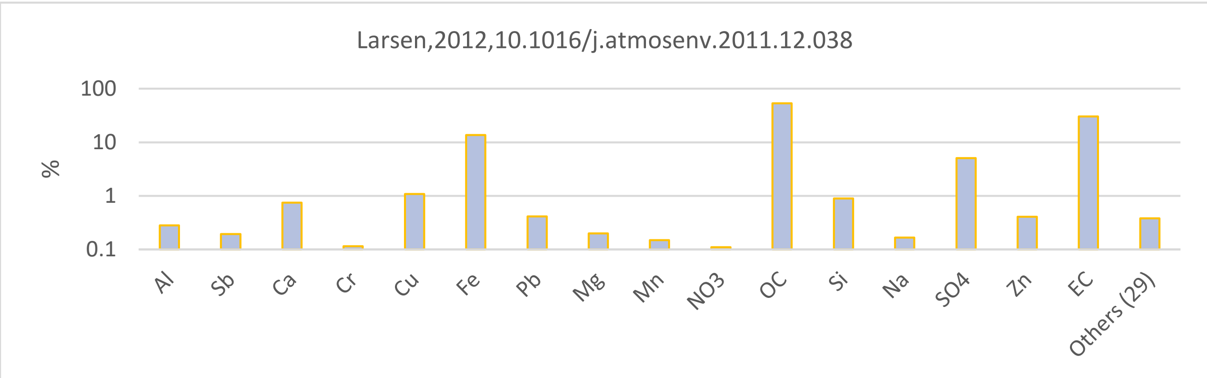


Figure 21. Exhaust diesel and gasoline chemical profile

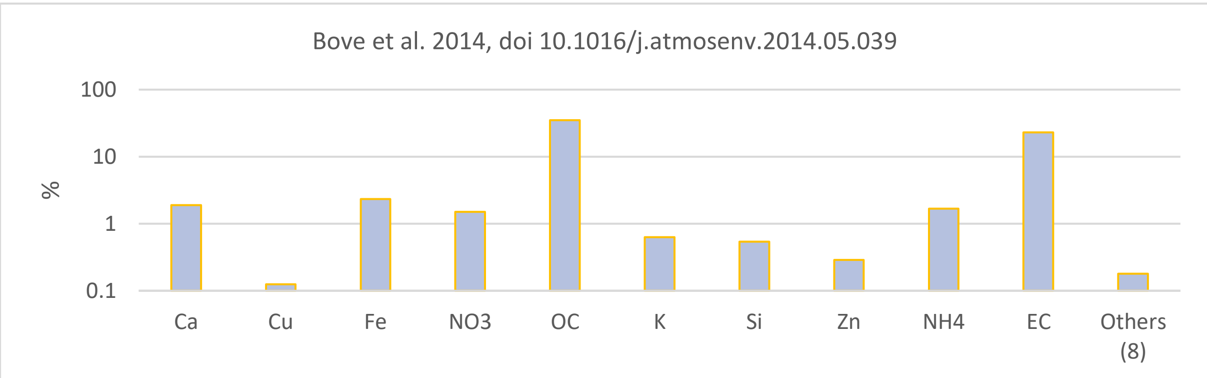


Figure 22. Urban traffic chemical profile

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.

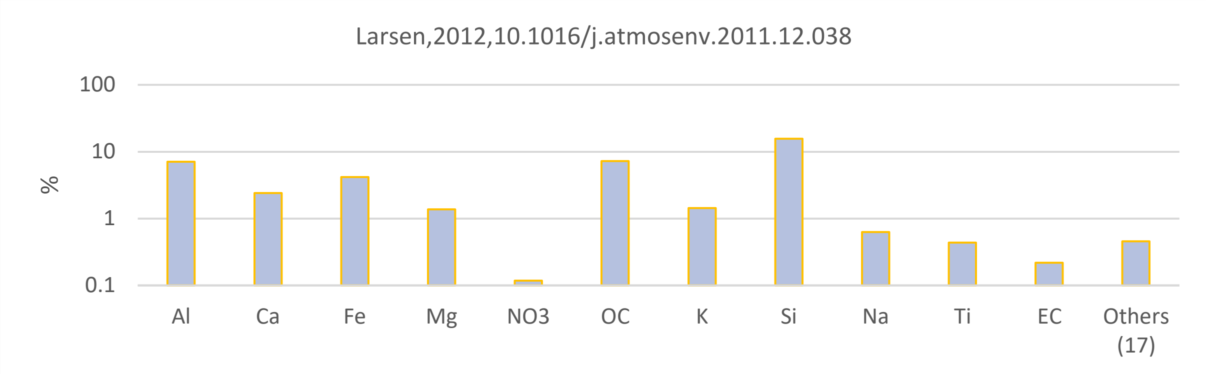


Figure 23. Road dust chemical profile

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.

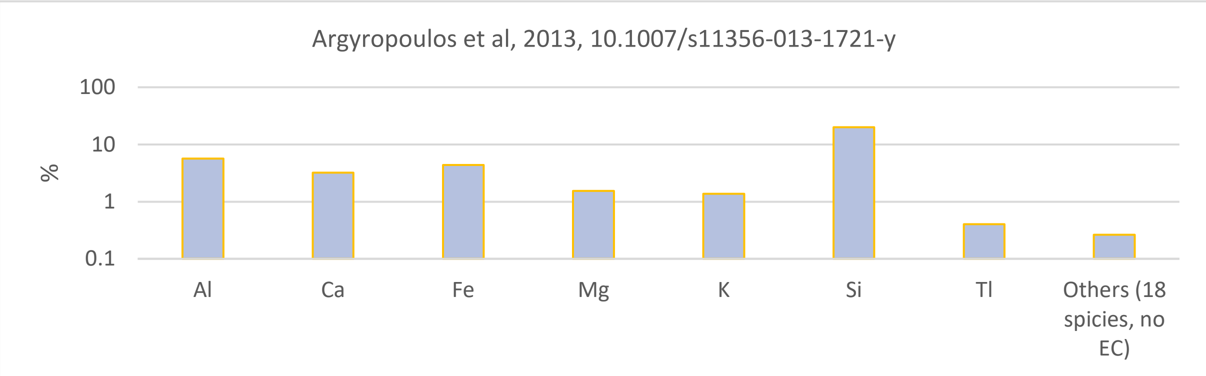


Figure 24. Soil dust chemical profile

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 %).

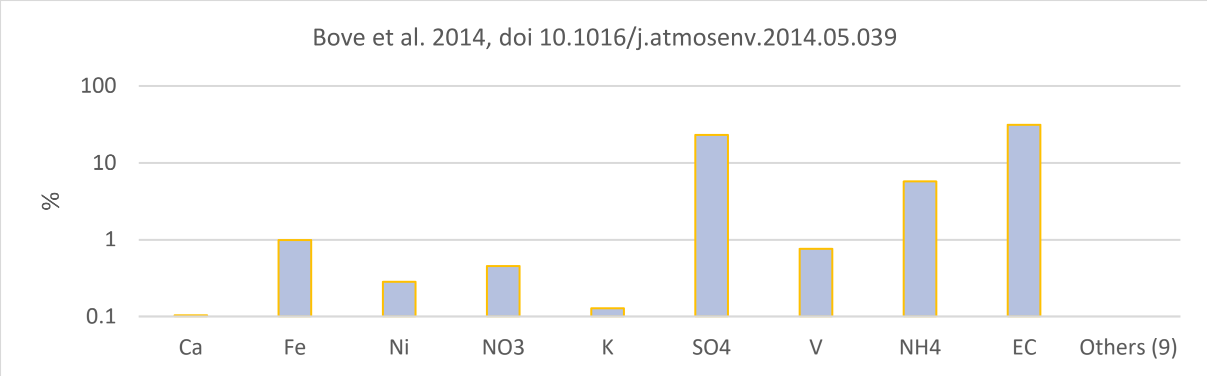


Figure 25. Residual oil chemical profile

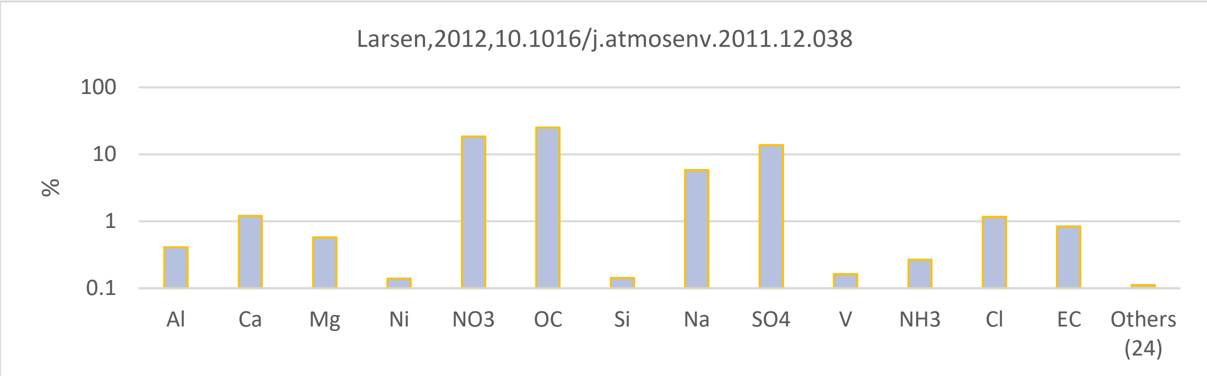


Figure 26. Fuel oil chemical profile

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

4. Particulate matter sampling and analysis

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

The sampling site in Strumica (our code MP2/AQP) is located adjacent to the state monitoring station for ambient air quality in Strumica. It is situated within the courtyard of the General Hospital, namely on the west side, at Panche Peshev bb street. The proximity to the nearest road is approximately 5 meters, while the distance from the main town square is approximately 500 meters.

The boiler station of the hospital's heating system is situated approximately 25 to 30 meters away and has an elevation of about 15 meters. The nearest residential buildings are located 20 meters from the station.

Figure 27. Monitoring location in Strumica urban area

The sampling program at this site commenced on March 11, 2023. A 24-hour sample was collected every other day, resulting in a total of 181 samples by March 26, 2024.

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

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

Sampling process was performed fully in line with the requirements of standard gravimetric measurement method for determination of the PM10/PM2,5 mass concentration of suspended particulate matter (EN 12341:2014). Sampling was performed on 47 mm PTFE filters (Advantec depth filter PF 020 and PF 040), according to Standard Operating Procedure of the UGD

AMBICON Lab, an ISO 17025 accredited for environment and samples from the environment testing (https://iarm.gov.mk/en/2021/07/01/lt-052-university-goce-delcev-shtip/).

Sampling procedure

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

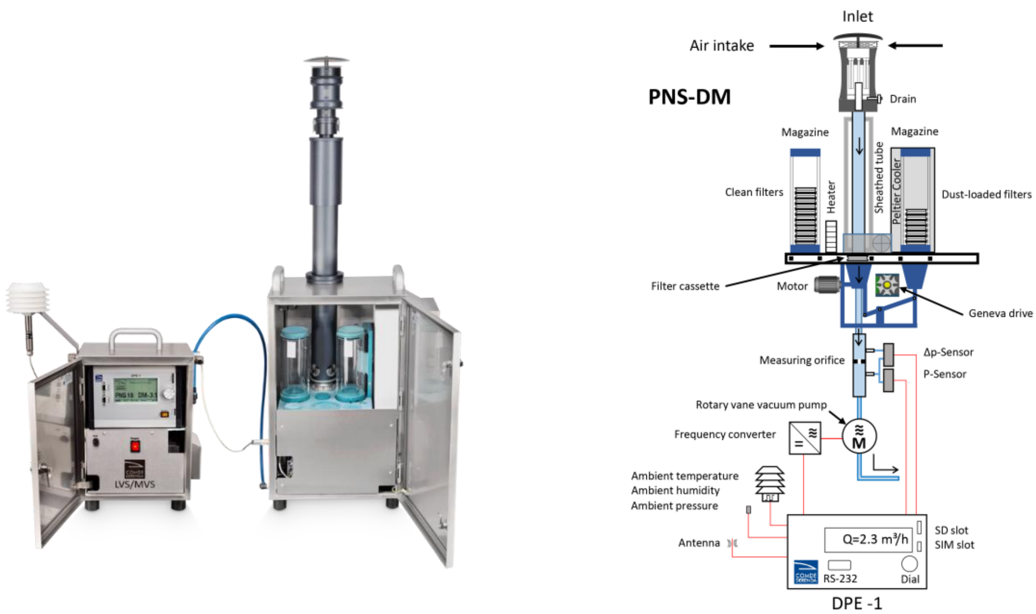


Figure 28. Sequential sampling system PNS 18T-DM 6.1

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 29. 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 $\mu g/m^3$, where the volume of air is that at the ambient conditions near the inlet during sampling.

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

4.2. Chemical speciation

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

Elemental analysis using energy dispersive X-ray fluorescence spectrometry

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

Figure 30. NEX CG by Rigaku

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.

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

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

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

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

Element	Certified reference concentration (ng/cm²)	Average	Standard deviation	Coefficient of variation (%)	Recovery (%)
Fe	733.14	728.86	14.74	2.02	100.0
Co	37.43	41.63	5.24	12.59	100.0
Ni	60.00	64.76	5.03	7.76	100.0
Cu	26.50	28.15	5.70	20.23	100.0
Zn	103.30	105.21	5.57	5.30	100.0
As	142.17	151.95	25.94	17.07	100.0
Se	88.00	89.06	5.35	6.01	100.0
Zr	20.50	21.17	1.04	4.92	100.0
Mo	18.79	18.80	0.53	2.81	100.0
Cd	440.71	482.71	48.49	10.05	100.0
Ba	75.29	74.83	4.54	6.07	100.0
Pb	210.00	195.13	15.68	8.04	100.0

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

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

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

Element	Zeta Score	Element	Zeta Score	Comments/Notes
Na	1.68	Ni	0.34	Explanation of Zeta-score values:
Mg	1.21	Cu	2.31	$\|z\| \leq 2.0$ the result is considered acceptable
Al	1.69	Zn	0.80	$2.0<\|z\|<3.0$ indicate a warning signal
Si	1.34	S	0,41	$\|z\|\geq 3.0$ results are considered unacceptable
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 31. 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 32. 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 Strumica, 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 (NH4+, $SO_4$2-, NO3-) and larger group of other elements (Na, Mg, P, S, Cl, K, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Ba, Pb).

Statistical Evaluation

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

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

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

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

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

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

Table 5. Statistical evaluation – Strumica dataset

	Units	N	Mean	SD	Minimum	Maximum	C.V.	95 th %	5 th %
PM2,5	μg/m³	181.0	42.7	34.6	6.7	239.6	81.0	108.0	10.6
Na	ng/m³	181.0	16.0	27.0	5.1	142.7	168.8	67.5	5.3
Mg		181.0	18.7	17.6	0.6	125.4	94.4	49.9	0.7
Al		181.0	116.8	107.8	0.4	815.3	92.3	311.1	14.9
Si		181.0	340.1	299.5	0.1	2203.5	88.1	861.3	46.3
P		181.0	2.1	1.3	0.0	8.3	62.3	4.3	0.4
S		181.0	168.9	111.1	0.2	881.4	65.8	331.9	30.1
Cl		181.0	32.8	61.6	0.1	492.5	187.7	158.0	0.2
K		181.0	334.8	386.2	37.5	2489.4	115.4	1265.2	68.8
Ca		181.0	512.1	386.1	14.9	2394.3	75.4	1089.8	123.7
Ti		181.0	22.9	18.2	1.0	141.9	79.7	51.9	4.9
V		181.0	2.7	2.3	0.6	17.5	85.4	6.8	0.6
Cr		181.0	0.7	0.6	0.4	5.2	94.6	1.6	0.4
Mn		181.0	5.6	3.9	0.5	27.3	68.9	12.4	1.3
Fe		181.0	217.9	180.6	0.9	1390.3	82.9	502.2	39.9
Co		181.0	12.7	9.7	0.4	73.8	76.2	28.9	3.0
Ni		181.0	2.2	0.5	2.0	5.5	23.3	2.2	2.1
Cu		181.0	4.3	2.1	1.8	14.6	50.0	8.4	1.9
Zn		181.0	28.0	25.1	2.2	181.0	89.8	69.8	4.8
As		181.0	0.8	0.4	0.2	3.6	51.4	1.4	0.2
Se		181.0	2.0	0.9	1.4	4.6	44.3	4.0	1.5
Br		181.0	2.2	1.1	0.6	10.8	52.3	3.8	0.7
Rb		181.0	2.0	1.3	0.6	8.9	63.1	4.1	0.6
Sr		181.0	10.1	10.9	0.1	131.8	108.3	18.1	1.3
Zr		181.0	4.2	2.4	0.0	14.2	56.4	8.5	1.0
Mo		181.0	1.9	1.3	0.0	10.0	65.6	3.8	0.3
Cd		181.0	1.3	1.5	0.1	9.5	116.8	4.8	0.3
Ba		181.0	27.1	21.7	1.2	168.5	80.0	62.1	5.6
Pb		181.0	8.3	5.3	3.6	39.2	63.9	15.5	3.7
EC		181.0	10736.5	5126.6	453.0	21200.0	47.7	21198.0	2263.0
NH_4		181.0	659.3	505.9	36.4	4468.5	76.7	1476.5	109.1
SO_4		181.0	4247.5	5087.0	245.4	43219.0	119.8	11574.3	797.1
NO_3		181.0	1159.2	1858.2	8.7	13805.5	160.3	4683.4	9.1

Table 6. Corelation matrix – Strumica dataset

	$PM_{2.5}$	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	NH_4	SO_4	NO_3
$PM_{2.5}$	1.00																																
Na	0.51	1.00																															
Mg	0.10	0.60	1.00																														
Al	0.05	0.54	0.99	1.00																													
Si	0.03	0.54	0.99	1.00	1.00																												
P	0.12	0.61	0.91	0.88	0.89	1.00																											
S	0.50	0.50	0.44	0.36	0.35	0.56	1.00																										
Cl	0.71	0.73	0.10	0.01	0.00	0.19	0.56	1.00																									
K	0.78	0.71	0.21	0.13	0.12	0.28	0.67	0.89	1.00																								
Ca	0.29	0.73	0.83	0.81	0.83	0.83	0.39	0.31	0.41	1.00																							
Ti	0.08	0.57	0.97	0.98	0.99	0.87	0.34	0.04	0.16	0.85	1.00																						
V	0.11	0.57	0.96	0.96	0.96	0.86	0.36	0.08	0.19	0.83	0.97	1.00																					
Cr	0.05	0.52	0.84	0.86	0.85	0.73	0.27	0.00	0.11	0.69	0.84	0.83	1.00																				
Mn	0.19	0.64	0.95	0.95	0.96	0.88	0.42	0.16	0.29	0.88	0.96	0.93	0.81	1.00																			
Fe	0.05	0.54	0.97	0.99	0.99	0.87	0.31	0.00	0.12	0.83	0.99	0.96	0.85	0.96	1.00																		
Co	0.08	0.56	0.97	0.98	0.98	0.86	0.35	0.04	0.17	0.84	0.98	0.96	0.85	0.98	0.99	1.00																	
Ni	0.22	0.21	0.21	0.20	0.19	0.20	0.31	0.21	0.21	0.16	0.19	0.21	0.19	0.22	0.19	0.22	1.00																
Cu	0.38	0.42	0.39	0.35	0.33	0.36	0.49	0.41	0.44	0.37	0.36	0.37	0.31	0.42	0.34	0.37	0.33	1.00															
Zn	0.64	0.46	0.10	0.05	0.04	0.13	0.51	0.67	0.68	0.24	0.08	0.10	0.03	0.18	0.06	0.09	0.25	0.40	1.00														
As	0.63	0.46	0.15	0.08	0.07	0.17	0.56	0.69	0.67	0.16	0.09	0.11	0.04	0.20	0.07	0.11	0.27	0.48	0.75	1.00													
Se	0.06	0.13	0.19	0.17	0.16	0.18	0.19	0.13	0.12	0.17	0.15	0.16	0.08	0.19	0.15	0.20	0.20	0.20	0.13	0.16	1.00												
Br	0.64	0.49	0.16	0.09	0.08	0.19	0.58	0.71	0.69	0.18	0.09	0.12	0.04	0.21	0.07	0.12	0.27	0.49	0.76	0.98	0.20	1.00											
Rb	0.61	0.59	0.29	0.22	0.21	0.26	0.52	0.70	0.76	0.39	0.23	0.23	0.19	0.39	0.21	0.30	0.28	0.45	0.53	0.59	0.34	0.61	1.00										
Sr	0.44	0.47	0.29	0.23	0.21	0.28	0.53	0.57	0.51	0.27	0.23	0.24	0.22	0.33	0.21	0.29	0.47	0.50	0.46	0.54	0.34	0.59	0.72	1.00									
Zr	0.21	0.63	0.87	0.82	0.83	0.98	0.70	0.30	0.39	0.79	0.80	0.80	0.67	0.83	0.80	0.80	0.24	0.41	0.22	0.26	0.21	0.29	0.35	0.36	1.00								
Mo	0.50	0.50	0.44	0.36	0.35	0.56	1.00	0.56	0.67	0.40	0.34	0.36	0.27	0.42	0.31	0.35	0.31	0.49	0.51	0.56	0.19	0.58	0.52	0.53	0.70	1.00							
Cd	0.77	0.72	0.23	0.15	0.14	0.29	0.67	0.89	1.00	0.43	0.18	0.20	0.12	0.31	0.14	0.19	0.21	0.44	0.67	0.66	0.13	0.68	0.77	0.52	0.40	0.67	1.00						
Ba	0.09	0.57	0.97	0.98	0.99	0.87	0.34	0.04	0.16	0.85	1.00	0.97	0.85	0.96	0.99	0.99	0.20	0.36	0.08	0.09	0.16	0.10	0.23	0.23	0.80	0.34	0.18	1.00					
Pb	0.57	0.48	0.17	0.11	0.10	0.15	0.43	0.64	0.60	0.27	0.12	0.15	0.11	0.23	0.09	0.17	0.26	0.40	0.53	0.58	0.28	0.60	0.74	0.64	0.23	0.43	0.61	0.12	1.00				
EC	0.19	-0.02	0.00	0.02	0.01	-0.07	-0.06	-0.01	0.04	-0.01	0.03	0.05	-0.02	0.05	0.03	0.05	-0.02	0.05	0.17	0.15	0.01	0.12	0.15	0.08	-0.08	-0.06	0.04	0.03	0.15	1.00			
NH_4	0.41	0.18	0.06	0.02	0.00	0.15	0.70	0.42	0.42	0.01	0.00	0.00	0.02	0.09	0.00	0.04	0.32	0.41	0.45	0.51	0.15	0.52	0.45	0.56	0.28	0.70	0.40	0.01	0.42	0.08	1.00		
SO_4	0.38	0.26	0.08	0.05	0.04	0.12	0.36	0.34	0.46	0.16	0.04	0.02	0.05	0.10	0.04	0.05	0.07	0.17	0.30	0.24	-0.05	0.24	0.29	0.12	0.18	0.36	0.45	0.04	0.21	0.18	0.38	1.00	
NO_3	0.72	0.52	-0.03	-0.08	-0.09	0.05	0.46	0.78	0.78	0.24	-0.04	-0.03	-0.04	0.08	-0.06	-0.03	0.23	0.39	0.64	0.60	0.08	0.61	0.64	0.52	0.15	0.46	0.77	-0.03	0.62	0.24	0.58	0.50	1.00

Temporal variations

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

Temporal variations are assessed using gravimetric data in conjunction with real-time data from collocated referent monitoring stations. Modelling was conducted using the Openair R package, which is designed for analysing air quality data, or more broadly, atmospheric composition data. Academics, as well as the public and corporate sectors, widely use the package.

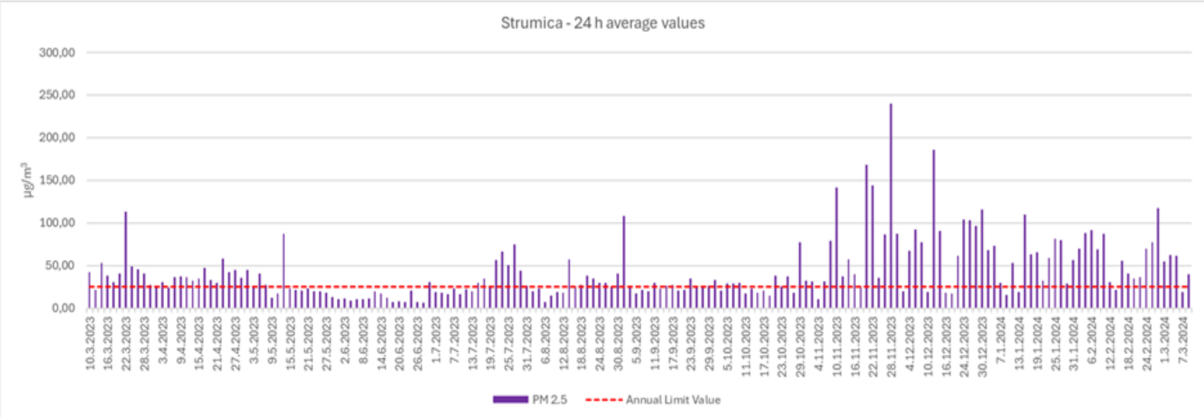


Figure 33. PM 2.5 – daily average concentrations from March 2023 to March 2024

The daily average PM2.5 concentrations measured at the Strumica monitoring site exhibit significant daily and seasonal variations, exceeding all national and European Union limits, targets, and thresholds for human health protection. Daily readings displayed considerable variability, with a standard deviation of 34.6 μg/m^3 and a coefficient of variation of 81 %. The concentrations ranged from a minimum of 6.7 μg/m^3 to a maximum of 239.6 μg/m^3, resulting in an average annual value of 42.7 μg/m^3, which exceeds the annual threshold limit value of 25 μg/m^3 by 71 %. The percentage of days surpassing the annual limit for PM2.5 (25 μg/m^3) was an alarming 63.5 % (115 out of 181 valid daily readings), with markedly elevated concentrations observed during the colder months (62.7 μg/m^3) compared to also high levels during the warmer season (27.6 μg/m^3). 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 other hand, although there are no significant differences between the days of the week, during the winter, there are pronounced 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 use of wood stoves and other solid fuel heating methods, which release substantial quantities of particulate matter into the atmosphere. The morning peak typically coincides with the start of daily activities, such as increased heating requirements, whereas the evening peak aligns with the return home and subsequent heating activities [19].

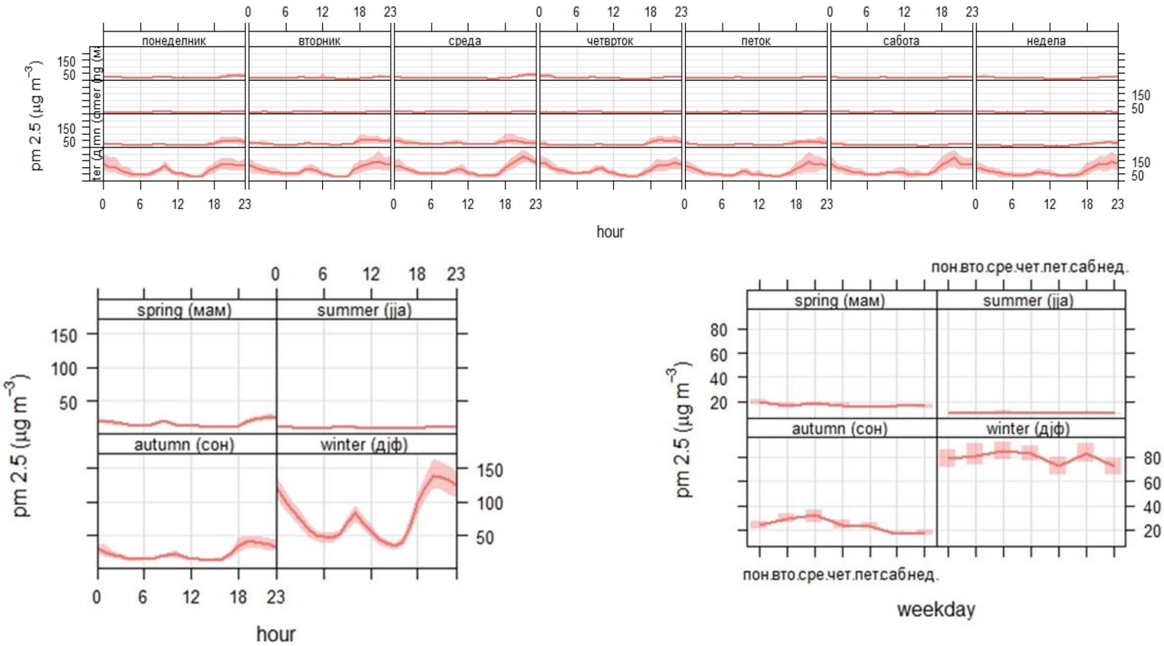


Figure 34. Daily variations in concentrations throughout all days, seasons, and weekdays

Correlation between meteorological conditions and PM concentrations

Bivariate polar plots serve as an effective analytical tool for understanding the origins and fluctuations of particulate matter, particularly finer fractions such as PM 2.5. These plots employ polar coordinates to depict the correlation between wind speed and direction, allowing researchers to visualize the influence of these meteorological variables on PM concentrations. The radial axis (represented by circles) typically indicates wind speed, while the angular axis denotes wind direction, facilitating the identification of major pollution sources based on their spatial distribution in relation to meteorological conditions.

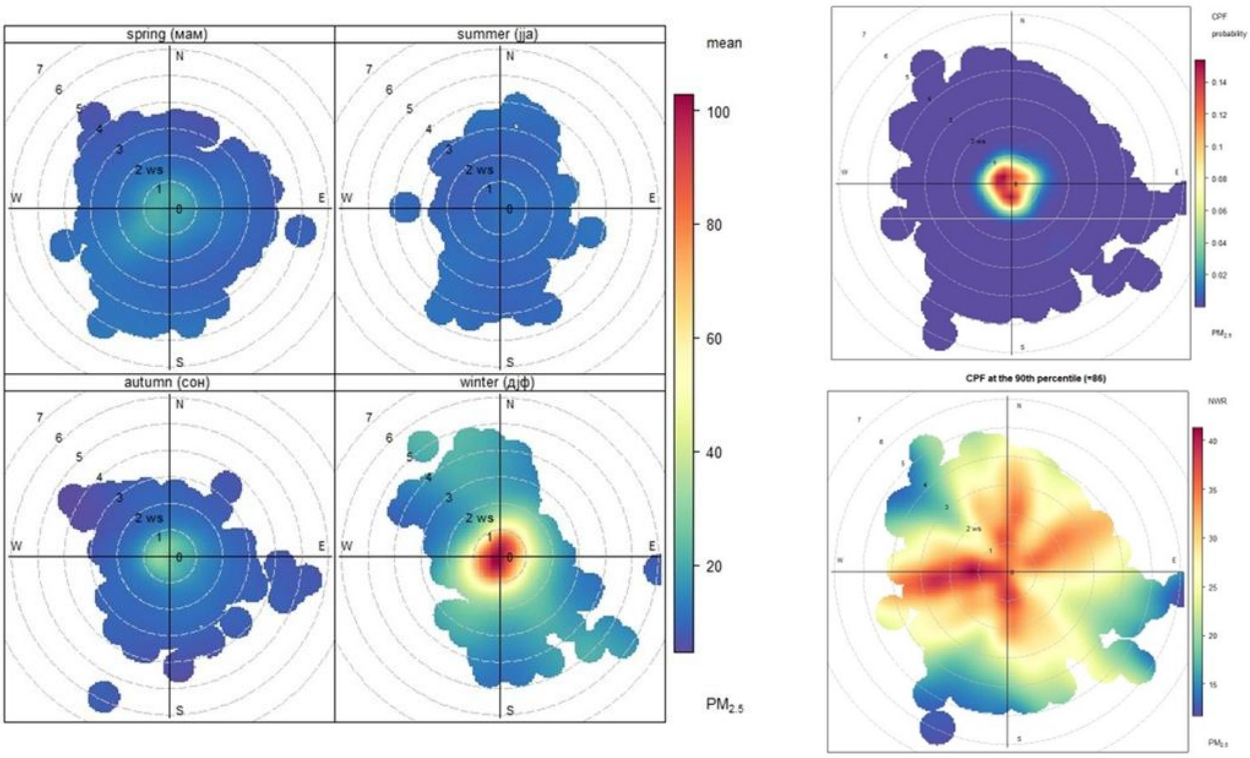


Figure 35. Bi-variate (seasonal), CPF and non paramteric polar plots

Polar plots for the Strumica area show that changes in concentration are mainly affected by local sources, as higher PM levels are only seen in winter and are mostly associated with low wind speeds (below 1 m/s). The conditional probability function plots back the assertion up by indicating that higher particulate matter levels are mostly related to low wind speeds, suggesting that these levels come from local or nearby sources.

Additionally, non-parametric wind regression (NWR) plots were used as a different way to better understand where pollution comes from in relation to wind patterns. This method uses nonparametric kernel smoothers that give more importance to pollution levels based on how close they are to certain wind speeds and directions. It shows that most pollution is linked to weak winds from all directions, indicating that the pollution is local.

The non-parametric regression identified the western part of the city and the village of Banica, the northern part and the village of Dobrejci, and the southern part and the village of Gradsko Baldovci as the most significant directions of pollution.

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, northwestern Europe has more nitrate, and southern Europe has more mineral dust in all fractions [20].

The results obtained for the Strumica urban area are similar to the results for the Skopje agglomeration. The contribution of mineral (soil) particles measured in Strumica is 3 % of total PM2.5 and is within the range identified in certain regions of Southern Europe [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.

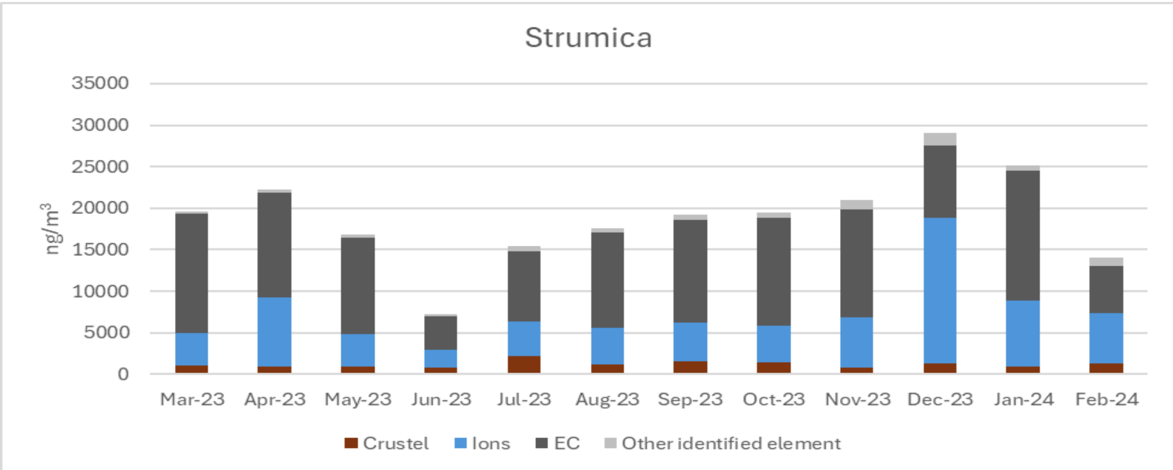
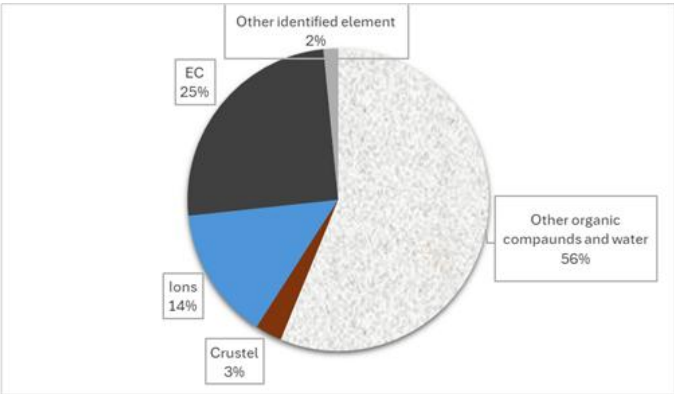


Figure 36. Major components and elemental groups identified

Sea salt contributions are negligible, as would be expected for a typically continental location. Contributions from ions such as sulphates and nitrates are significantly lower than values recorded across Europe, with 14 % of the combined contribution falling within the range of values recorded in Skopje [20, 21]. Although this could be attributed to several factors, it is important to note the relatively low average concentrations of their gaseous precursors, such as nitrous oxides.

Elemental carbon (EC) contributions in the urban area of Strumica exceed European averages, averaging 25 %. This figure significantly exceeds the values recorded in Central Europe and is somewhat higher than those observed in Skopje. This discrepancy likely reflects 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, also significantly impact this situation.



	Crustal	EC	Ions
N-W Europe	5	7	37
Southern Europe	11	8	22
Central Europe	5	14	32
Skopje	4	23	16
Strumica	3	25	14

Figure 37. Contribution of major particulate matter components [20, 21]

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

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

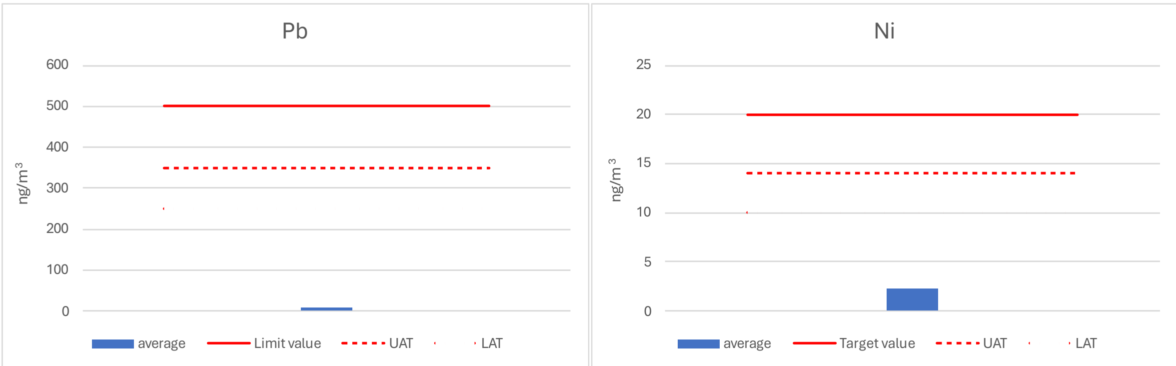


Figure 38. Average monthly concentrations of lead (Pb) and nickel (Ni) in Strumica

5. Positive Matrix Factorisation

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

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

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

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

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

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

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

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

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

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

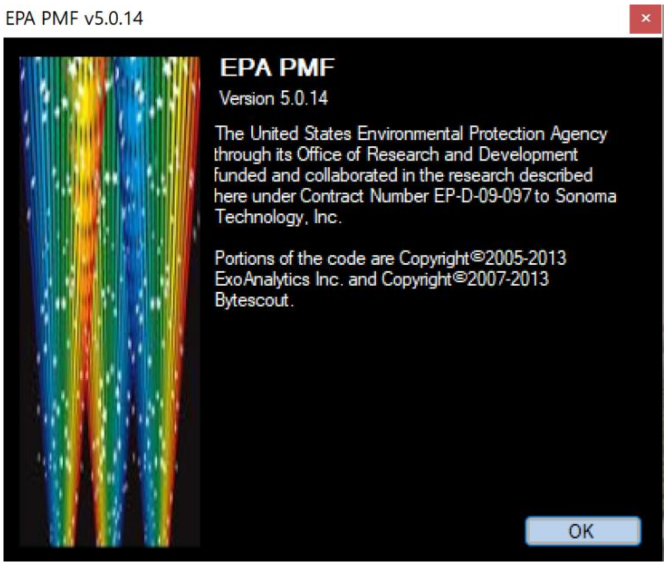


Figure 39. Free software US-EPA PMF 5.0 version 5.0.14 – splash screen

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

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

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

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

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

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

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

5.1. Input data and PMF model setting

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

Following the EU protocol for receptor models [32], the data were initially processed to remove values that could potentially degrade the quality of the analysis. To validate the data and identify atypical values when compared to the rest of the dataset, scatter plots and time series analysis were employed. After data validation, the original datasets included 32 species and 181 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 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 Strumica datasets included 6 factors. Factors were attributed to their sources though a quantitative and qualitative comparisons of the factor chemical profile with PM profiles reported EC-JRC SPECIEUROPE data base and profiles from previous source apportionment studies available in the literature.

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

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

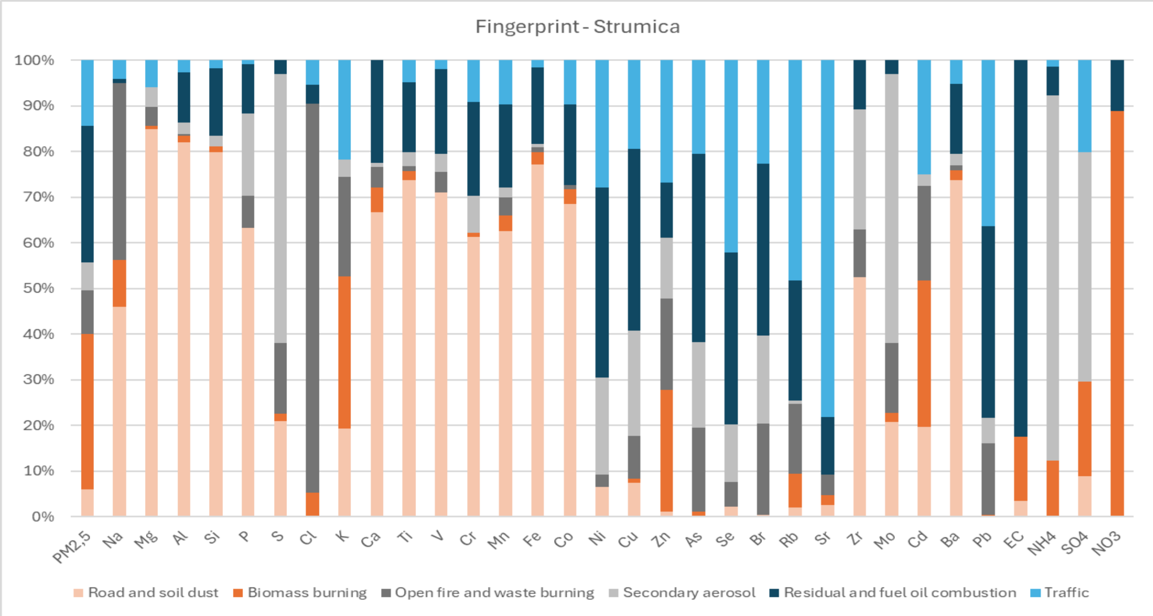


Figure 40. Factor fingerprint for Strumica

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, Chisinau, Zagreb and Krakow [39]. 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 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].

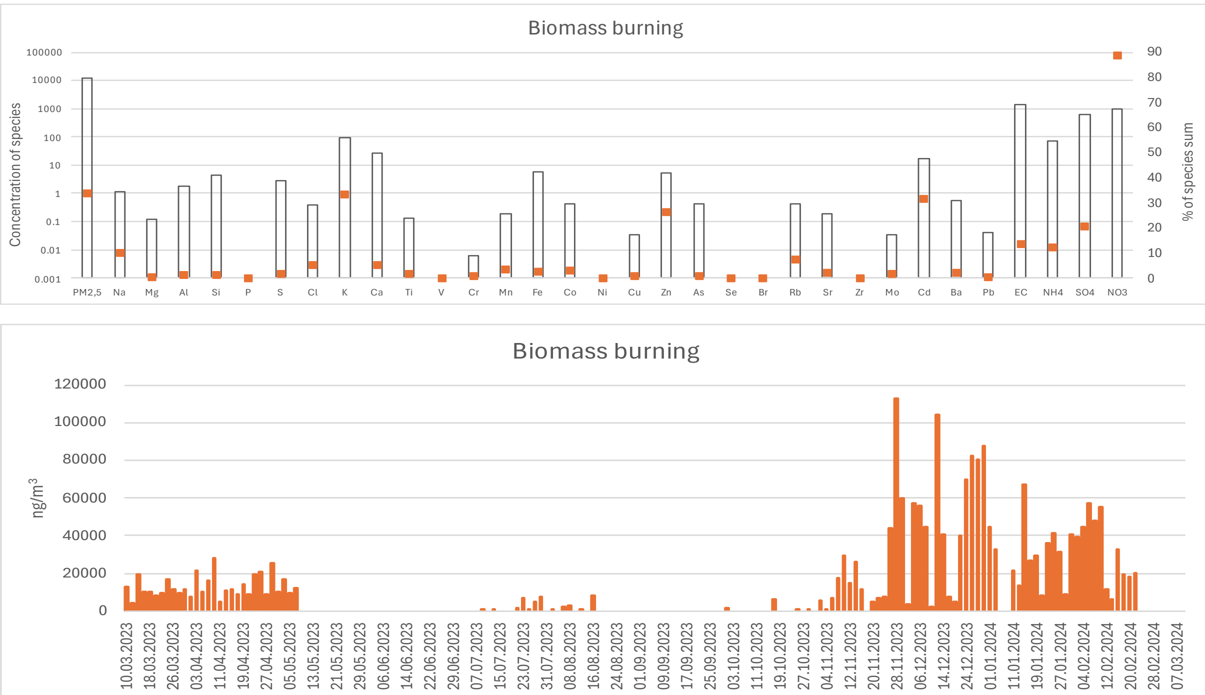


Figure 41. Biomass burning factor profiles in Strumica

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

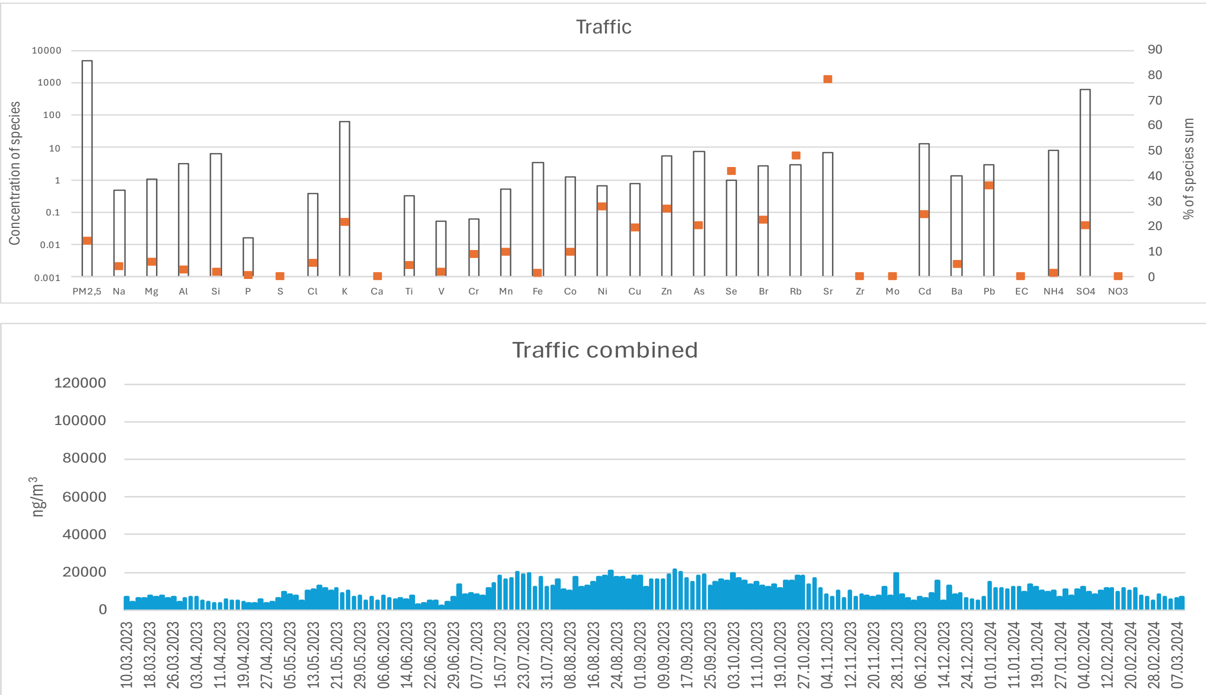


Figure 42. Traffic associated factors for Strumica dataset

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

Organic carbon, sodium, and water-soluble ions including nitrates and sulphates are common key species for fuel oil emissions. Water-soluble ions, V, Fe, and Ni are also important species for residual oil combustion, but increased quantities of elemental carbon, rather than organic carbon, are common for this source. Vanadium, either alone or in conjunction with nickel, is a prevalent marker in PMF source profiles, in most European and Central Asian urban areas [39].

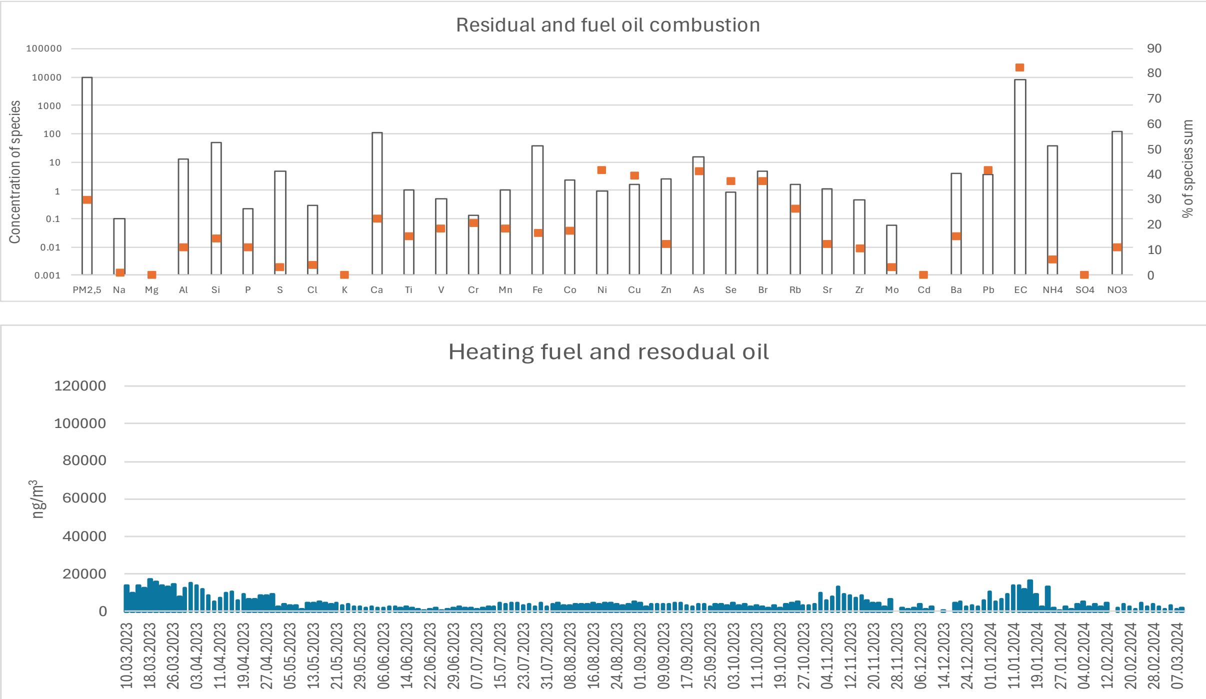


Figure 43. Fuel and residual oil factor profiles for Strumica urban area

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.

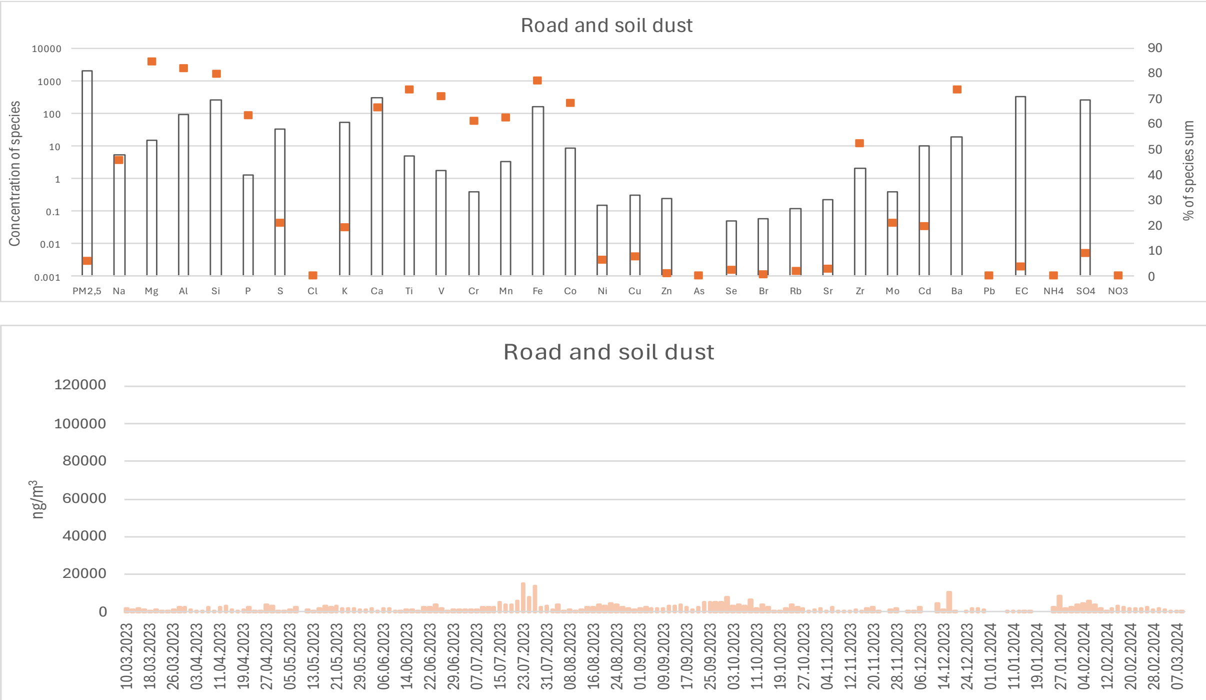


Figure 44. Mineral dust factor profiles for Strumica urban area

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.

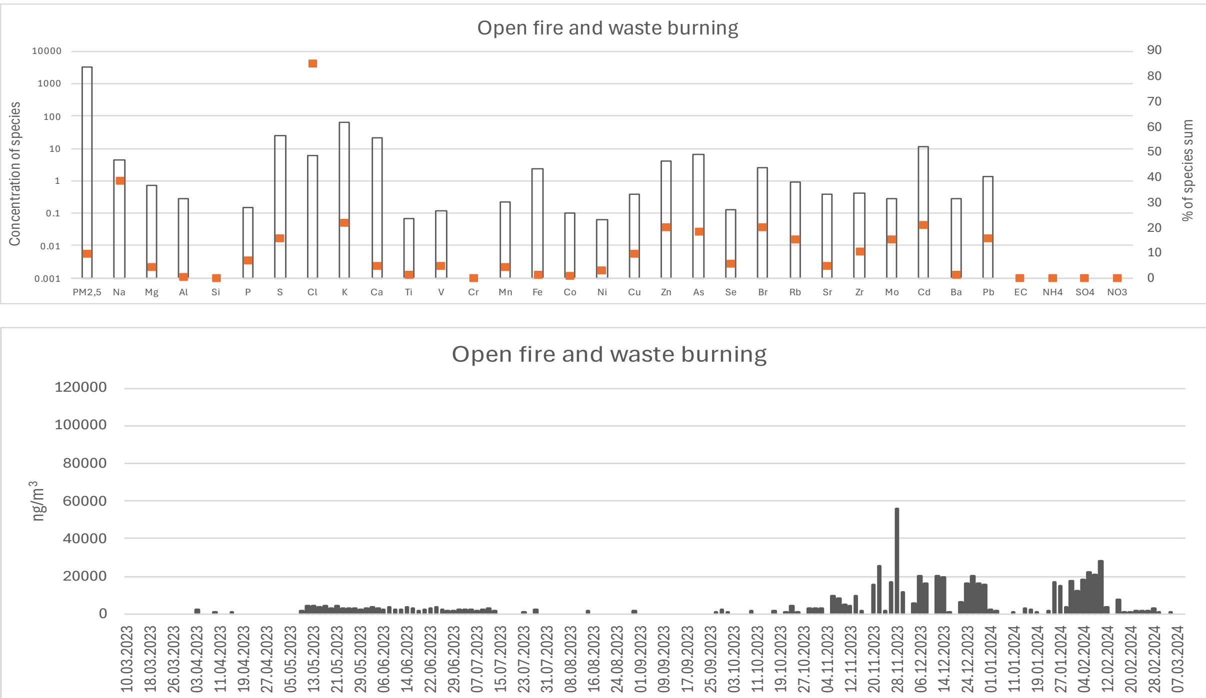
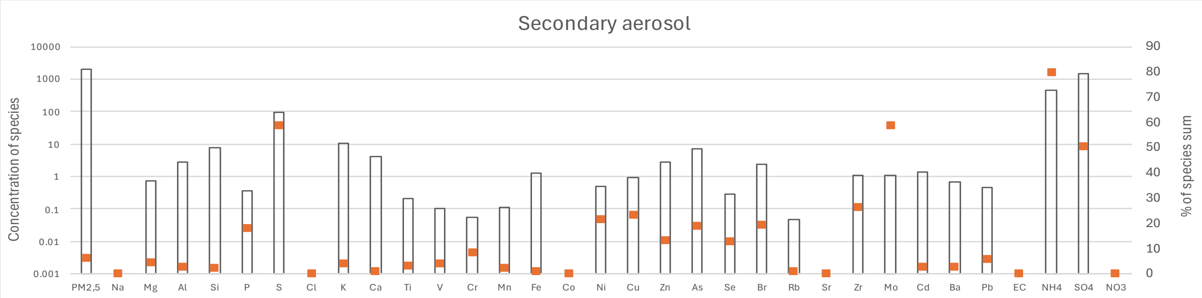


Figure 45. Open fire burning factor profile

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.



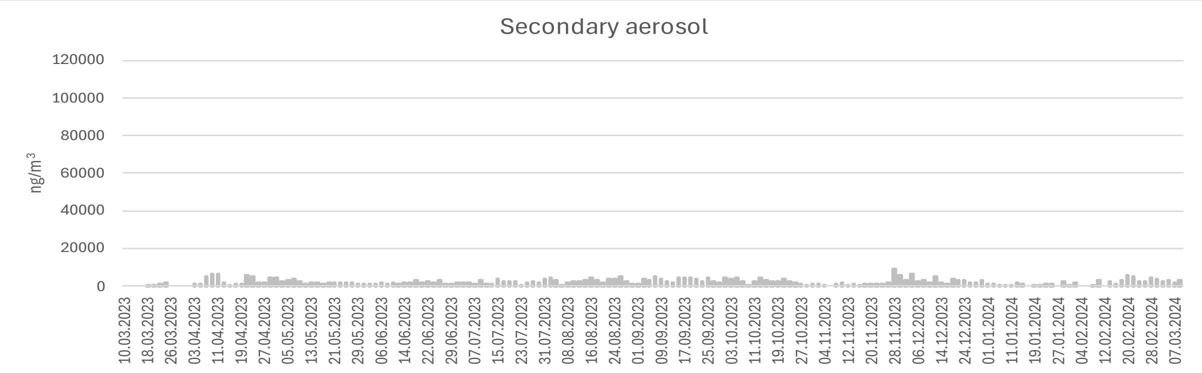


Figure 46. Secondary Aerosols factor profile

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 Strumica include biomass burning, open fires, waste burning, traffic, secondary aerosols, road dust, soil dust, and the combustion of fuel and residual oil. The traffic contribution was assessed by combining modeled values from two identified sources: traffic and the combustion of fuel and residual oil. Due to the similarity in exhaust emissions from older diesel vehicles and fuel oil-burning boilers, a significant portion (70 %) of fuel oil contributions during warmer periods is attributed to traffic sources.

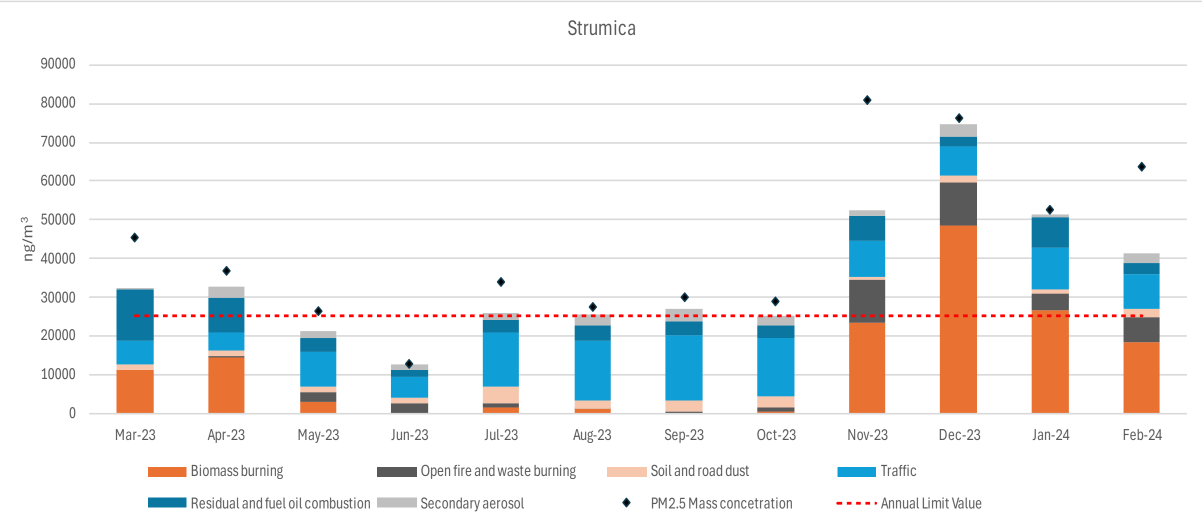


Figure 47. Average monthly contributions to total particulate mass (PM 2.5) – Strumica

Biomass burning was the most significant source in the municipality of Strumica during the winter months, with the largest contribution to total particle mass occurring in November, December, January, February, and March, while it had a minimal impact during the summer months. Biomass burning primarily pertains 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 11.2 to 48.6 μg/m^3. This source alone, during the winter season, exceeds the annual limit value for PM 2.5, which is set at 25 μg/m^3. The relative contributions of biomass burning to total particle mass demonstrate significant seasonal variability, with this source reaching up to 65.3 % during the winter months. Despite being entirely seasonal, biomass burning accounts for a substantial annual relative contribution of 35 %.

Annually, traffic represents the second largest source of air pollution, demonstrating a steady contribution throughout the year, with a notable increase during the summer and fall months, ranging from 4.5 to 16.7 μg/m^3. The annual relative contribution of traffic constituted 29 % of the total particulate mass (PM 2.5), with monthly relative contributions varying between 10.1% and 62.1%. This source includes emissions resulting from vehicle exhaust, brake, and tire wear, in addition to the combustion of oil in older diesel engines, such as those found in tractors, trucks, and passenger vehicles lacking exhaust control devices.

Road and soil dust, also referred to as mineral dust, comprises particulate matter primarily originating from construction activities and the resuspension of deposits on roadways. This source significantly contributes to total particulate mass (PM2.5), with an increasing contribution during dry seasons, ranging from 0.9 to 4.6 μg/m3. The monthly contributions from this source vary between 1.8 % and a significant 17.6 %, but the annual relative contribution reaches a noteworthy 6 %.

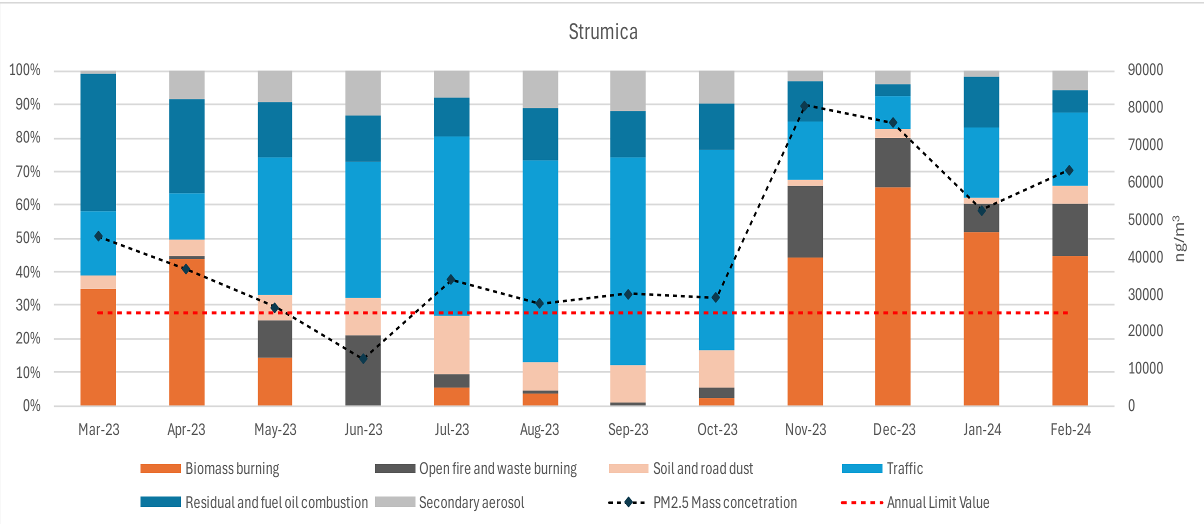


Figure 48. Relative monthly contribution – Strumica

Combustion of fuel and residual oil primarily originates from boilers used for heating public facilities and buildings (such as kindergartens, schools, and hospitals), as well as from industrial facilities for heat production or various technological processes. Fuel and residual oil contribute 1.8 and 13.2 μg/m^3 to the total particulate mass. This source is consistently present throughout the year. The annual relative contribution of fuel and residual oil combustion accounts for 15 % of the total particulate mass (PM2.5), with relative monthly contributions ranging from 3.4 % to 28 %.

Open fires and waste burning encompass the combustion of crop residue, agricultural and garden waste materials, as well as landfill fires and wildfires. This category also includes the burning of various waste materials in household stoves or small industrial boilers and is predominantly observed during the spring and early summer months, with increased activity noted in the autumn and winter periods. The average monthly contribution from this source reaches up to 11.2 μg/m^3. The monthly contribution from this source can be as high as 21 %, while the annual contribution stands at 9 %.

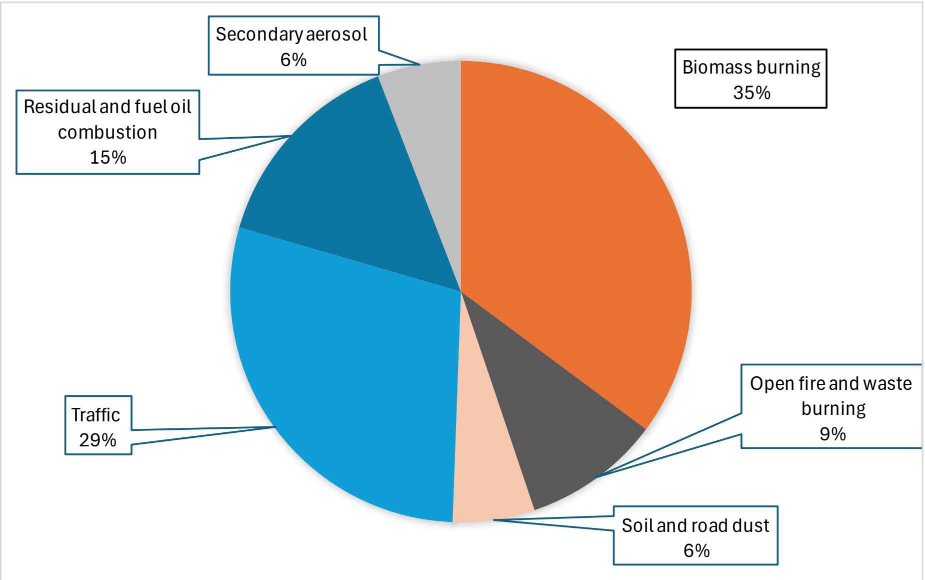


Figure 49. Relative annual contribution of PM 2.5 sources at Strumica

Secondary aerosols are particles that are not directly emitted but are generated by various chemical reactions in the atmosphere, influenced by sunlight, ozone, and humidity, ultimately resulting in the formation of "secondary aerosols." Secondary aerosols 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 annual relative contribution of secondary aerosols was 6 % of the total particle mass (PM2.5), with monthly contributions displaying significant variability, ranging from 0.8 % to 13.2 %.

6. Conclusions and recommendations

The urban region of Strumica suffers from poor air quality over an extended period. Particulate matter (PM10) concentrations consistently exceed established threshold limits. Between 2019 and 2023, Strumica's average annual PM10 concentrations and the number of exceedances of the 24-hour limit value have continuously exceeded the recommended levels.

The AMBICON Laboratory conducted this Source Apportionment Study to gather information on pollution sources and their contributions to ambient air pollution in Strumica. The activities followed the strict guidelines in the European handbook on air pollution source apportionment using receptor models (Revised edition 2019, JRC) and included a year-long program for collecting and analyzing air samples, which helped create a complex model to identify pollution sources. The sampling program commenced on March 10, 2023, and through the end of March 2024, 181 samples were collected, with a 24-hour sample taken every other day. The sampling process was executed in strict compliance with the standard gravimetric measurement method for determining the mass concentration of PM10/PM2.5 suspended particulate matter (EN 12341:2014). Energy dispersive X-ray fluorescence (ED-XRF) was used to analyze the elements, an optical transmissometer measured the amount of elemental carbon, and spectrophotometry helped identify water-soluble ions.

The daily average PM2.5 concentrations measured at the Strumica 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 6.7 $\mu g/m^3$ to a maximum of 240 $\mu g/m^3$, resulting in an average annual value of 42.7 $\mu g/m^3$, which significantly exceeds the annual threshold limit value of 25 $\mu g/m^3$ by staggering 71%. The percentage of days surpassing the annual limit for PM 2.5 (25 $\mu g/m^3$) was an alarming 63.5 % (115 out of 181 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 Strumica area demonstrate concentration variations influenced from local meteorological conditions, notably indicating that elevated PM concentrations are exclusively observed during the winter season and are predominantly linked to low wind speeds (1 to 2 m/s). Furthermore, non-parametric wind regression (NWR) plots demonstrates that the majority of pollution is associated only with weak winds from all directions, which indicates that the pollution is local (from the immediate surroundings), with the non-parametric regression defining the western part of the city and the village of Banica, the northern part and the village of Dobrejci, the eastern part, and the southern part with the zone of the village of Gradsko Baldovci 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 Strumica include biomass burning, open fire and waste burning, traffic, secondary aerosols, road and soil dust, and fuel and residual oil burning.

On annual level, biomass burning represents the primary air pollution source, and although entirely seasonal, biomass burning accounts for a significant annual relative contribution of 35% of the total particulate mass (PM 2.5). Traffic is second largest source, demonstrating a steady contribution throughout the year, with a notable increase during the summer and fall months. The annual relative contribution of traffic constituted 29 % of the total particulate mass (PM 2.5) with monthly relative contributions varying between 10.1 % and 62.1 %. The combustion of fuel and residual oil primarily originates from boilers in industrial facilities for heat generation or other technological operations, with a smaller contribution from boilers used for heating public facilities and buildings such as kindergartens, schools, and hospitals. This source occurs consistent over the year. Annual relative contribution of fuel and residual oil combustion accounted for 15 % of the total particulate mass (PM 2.5) mass.

The annual relative contribution of open fires and waste burning constituted 9 % and road and soil dust and secondary aerosol each constituted 6% of the total particulate mass (PM 2.5).

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

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

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

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

Lessons learned

Lesson No. 1	Solutions available
The widespread use of biomass as the primary energy source for residential heating is the predominant contributor to fine particulate matter (PM2.5) in most urban areas across the country. According to the latest data, at least 57 % of households in Strumica (or 10,048 households) utilize firewood as the main heating source, accounting for 79 % of total PM2.5 primary emissions and directly contributing up to 62% of the total particulate mass throughout several months of the heating season. Unfortunately, the efficiency coefficient of the latest wood-burning stoves available in our country is only 0.75. In addition to their comparatively low efficiency coefficient, 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.
Lesson No. 2	Solutions available
Small boilers used in small-scale manufacturing plants or workshops, as well as greenhouse heating, can be a substantial source of pollution if not properly regulated and monitored, particularly in commercially active locations such as Strumica. The municipality of Strumica is known for its active and vibrant economy. This area is one of the largest producers of vegetables in controlled environments (greenhouses), with several thousand hectares of covered land. There are hundreds, if not thousands, of small boilers that create heat for greenhouses, space heating, and other production needs. The majority of these units are old and inefficient boilers that typically burn low-quality solid fuels, including agricultural and other types of waste, resulting in a significant and specific source of pollution that is almost uncontrolled and difficult to identify because the specific chemical fingerprints mix with a variety of sources such as biomass burning (in the residential sector), industry, and open fire waste burning.	Small solid fuel boilers used in manufacturing plants or greenhouses are principally regulated by the Eco-design Directive and the Energy Labelling Regulation, which aims to improve energy efficiency and limit pollutant emissions from such appliances. Strict adherence to these standards, which have been necessary in the EU since 2020, is likely to considerably improve current problems. Innovative ways that harness the potential of numerous sustainable heating technologies such as geothermal energy, waste heat recovery, heat pumps, and combined heat and power plants, can transform greenhouse agriculture into a more environmentally friendly industry. Adopting such innovations not only reduces environmental effect but also improves economic viability and resilience in agricultural operations. Positive examples can be found across the globe. Dutch greenhouses maintain appropriate temperatures without the use of fossil fuels by drawing heat from deep underground water reservoirs. This technique not only cuts carbon emissions but also

	provides a consistent and reliable energy source. In the United Kingdom, Low Carbon Farming pioneered the use of waste heat from water treatment facilities to heat large-scale greenhouses. Horticultural enterprises in Straelen, Germany, have transitioned away from fossil fuels by using heat pump-based heating systems demonstrating viability of this systems, that not only decrease emissions. but it also proves cost-effective in the long run. Producers in West Sussex, UK, use combined heat and power (CHP) plants to provide the necessary electricity and heat, allowing them to produce vegetables even throughout the cold winter season.

References

1. Plan for reducing pollution and improving ambient air quality 2025-2029, Municipality of Strumica
2. Available at the link: https://en-gb.topographic-map.com/map-z7851/Strumica/
3. Available at the link: https://strumica.gov.mk/prirodni-karakteristiki/
4. Energy Efficiency Strategy of the Municipality of Strumica 2019 – 2023, February, 2019, available at the link: https://strumica.gov.mk/wp-content/uploads/2022/04/EE-Strumica-2019-2023.pdf
5. MakStat Database, Available at the link: https://makstat.stat.gov.mk/PXWeb/pxweb/mk/MakStat/
6. Study for the establishment of public urban transport in Strumica, MS Stop DOOEL Strumica, 2024
7. Rickly, P. S., Guo, H., Campuzano-Jost, P., Jiménez, J. L., Wolfe, G. M., Bennett, R., ... & Rollins, A. W. (2022). Emission factors and evolution of SO2 measured from biomass burning in wild and agricultural fires. https://doi.org/10.5194/acp-2022-309
8. Ren, Y., Shen, G., Shen, H., Zhong, Q., Xu, H., Meng, W., ... & Tao, S. (2021). Contributions of biomass burning to global and regional so2 emissions. Atmospheric Research, 260, 105709. https://doi.org/10.1016/j.atmosres.2021.105709
9. Ahn, K., Shin, D., Lee, Y., Jeong, Y., Jung, J., & Kim, H. (2023). Biochar production and demineralization characteristics of food waste for fuel conversion. Molecules, 28(16), 6114. https://doi.org/10.3390/molecules28166114
10. Available at the link: https://source-apportionment.jrc.ec.europa.eu/Specieurope/index.aspx
11. EMEP/EEA air pollutant emission inventory guidebook 2023, available at the link: https://www.eea.europa.eu/en/analysis/publications/emep-eea-guidebook-2023
12. Pernigotti, D., Belis, C.A., Spanó, L., 2016. SPECIEUROPE: The European data base for PM source profiles. Atmospheric Pollution Research, 7 (2), pp. 307-314. DOI: 10.1016/j.apr.2015.10.007
13. Rigaku NEX CG, website: https://www.rigaku.com/products/edxrf/nexcg
14. Standard Operating Procedure for PM2.5 Cation Analysis, revision 7, August 2009, Environmental and Industrial Sciences Division RTI International, Research Triangle Park, North Carolina
15. Guo, H., Gu, X., Ma, G., Shi, S., Wang, W., Zuo, X., ... & Zhang, X. (2019). Spatial and temporal variations of air quality and six air pollutants in China during 2015–2017. Scientific Reports, 9(1). https://doi.org/10.1038/s41598-019-50655-6
16. Thabethe, N. D., Makonese, T., Masekameni, D., & Brouwer, D. (2024). Diurnal and seasonal variations of particulate matter (PM 2.5) at a tailing storage facility and nearby community. https://doi.org/10.21203/rs.3.rs-3875400/v1
17. Yorkor, B., Leton, T. G., & Ugbebor, J. N. (2021). Analysis of temporal variations of air pollutant concentrations in ogoni area, niger delta region, nigeria. Asian Journal of Environment &Amp; Ecology, 63-73. https://doi.org/10.9734/ajee/2021/v16i430260
18. Onanuga, K., Daniel, V., Mustapha, A., & Maitera, O. (2024). Seasonal variations assessment of air pollutants of communities in the vicinity of scrap metal recycling industries in ogijo, shagamu south lga, ogun state, sw nigeria. Asian Journal of Applied Chemistry Research, 15(1), 37-47.

19. Liu, X., Wei, Y., Liu, X., Zu, L., Wang, B., Wang, S., ... & Zhu, R. (2022). Effects of winter heating on urban black carbon: characteristics, sources and its correlation with meteorological factors. Atmosphere, 13(7), 1071. https://doi.org/10.3390/atmos13071071

20. Putaud, J.P., Van Dingenen, R., Alaustey, A., Bauer, H., Birmili,W., et al., 2010. A European aerosol phenomenology – 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos. Environ. 44, 1308–1320.

21. Source Apportionment Study for Skopje urban area – identification of main sources of ambient air pollution, AMBICON Lab, Goce Delcev University, Stip, North Macedonia

22. Norris, G., R. Duvall, S. Brown, AND S. Bai. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-14/108 (NTIS PB2015-105147), 2014.

23. Lee E, Chan C.K., Paatero P., (1999). Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. Atmospheric Environment, 33, 3201–3212.

24. Polissar A.V., Hopke P.K., Paatero P., Kaufmann Y.J., Hall D.K., Bodhaine B.A., Dutton E.G., Harris J.M., (1999). The aerosol at Barrow, Alaska: long-term trends and source locations. Atmospheric Environment, 33, 2441–2458.

25. Sukon Aimanant & Paul J. Ziemann (2013) Development of Spectrophotometric Methods for the Analysis of Functional Groups in Oxidized Organic Aerosol, Aerosol Science and Technology, 47:6, 581-591, DOI: 10.1080/02786826.2013.773579

26. Xie Y., Berkowitz C.M., (2006). The use of positive matrix factorization with conditional probability functions in air quality studies: an application to hydrocarbon emissions in Houston, Texas. Atmospheric Environment, 40, 3070–3091.

27. Begum B.A., Kim E., Biswas S.K., Hopke P.K., (2004). Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh. Atmospheric Environment, 38, 3025-3038.

28. Bzdusek P.A., Christensen E.R., Lee C.M., Pakadeesusuk U., Freedman D.C., (2006). PCB congeners and dechlorination in sediments of Lake Hartwell, South Carolina, determined from cores collected in 1987 and 1988. Environmental Science and Technology, 40, 109–119.

29. Singh K.P., Malik A., Singh V.K., Sinha S., (2006). Multi-way data analysis of soils irrigated with wastewater. A case study. Chemometrics and Intelligent Laboratory Systems, 83, 1-12.

30. Soonthornnonda P., Christensen E.R., (2008). Source apportionment of pollutants and flows of combined sewer wastewater. Water Research, 42, 1989–1998.

31. Hopke P.K., (2003). Recent developments in receptor modeling. Journal of chemometrics, 17, 255–265.

32. Belis C.A., Favez O., Mircea M., Diapouli E., Manousakas M-I., Vratolis S., Gilardoni S., Paglione M., Decesari S., Mocnik G., Mooibroek D., Salvador P., Takahama S., Vecchi R., Paatero P., European guide on air pollution source apportionment with receptor models - Revised version 2019, EUR 29816 EN, Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-76-09001-4, doi:10.2760/439106, JRC117306.

33. Polissar, A. V., Hopke, P. K., & Poirot, R. L. (2001). Atmospheric aerosol over Vermont: chemical composition and sources. Environmental science & technology, 35(23), 4604–4621. https://doi.org/10.1021/es0105865

34. Mirakovski, D., Zendelska, A., Boev, B. et al. Evaluation of PM2.5 Sources in Skopje Urban Area Using Positive Matrix Factorization. Environ Model Assess 29, 1–14 (2024). https://doi.org/10.1007/s10666-024-09961-1

35. H. Simon, L. Beck, P.V. Bhave, F. Divita, Y. Hsu, D. Luecken, J.D. Mobley, G.A. Pouliot, A. Reff, G. Sarwar, M. Strum, The development and uses of EPA's SPECIATE database, Atmos. Pollut. Res. (2010), pp. 196-206, 10.5094/APR.2010.026

36. Zhang, X., Hecobian, A., Zheng, M., Frank, N. H., and Weber, R. J.: Biomass burning impact on PM2.5 over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, Atmos. Chem. Phys., 10, 6839-6853, 10.5194/acp-10-6839-2010, 2010.

37. Lee, S., Liu, W., Wang, Y., Russell, A. G., and Edgerton, 948 E. S.: Source apportionment of PM 2.5: Comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States, Atmos. Environ., 42, 4126-4137, 2008.

38. Duvall, R. M., Majestic, B. J., Shafer, M. M., Chuang, P. Y., Simoneit, 846 B. R. T., and Schauer, J. J.: The water-soluble fraction of carbon, sulfur, and crustal elements in Asian aerosols and Asian soils, Atmos. Environ., 42, 5872-5884, https://doi.org/10.1016/j.atmosenv.2008.03.028, 2008.

39. Almeida et al. (2020) Ambient particulate matter source apportionment using receptor modelling in European and Central Asia urban areas, Environmental Pollution, Volume 266, Part 3, https://doi.org/10. 1016/j.envpol.2020.115199

40. Sun, Y., Zhuang, G., Tang, A., Wang, Y., and An, Z.: Chemical Characteristics of PM2.5 and PM10 in Haze−Fog Episodes in Beijing, Environ. Sci. Technol., 40, 3148-3155, 10.1021/es051533g, 2006.

41. Zhou, Y., Zheng, N., Luo, L., Zhao, J., Qu, L., Guan, H., Xiao, H., Zhang, Z., Tian, J., and Xiao, H.: Biomass burning related ammonia emissions promoted a self-amplifying loop in the urban environment in Kunming (SW China), Atmos. Environ., 118138, https://doi.org/10.1016/j.atmosenv.2020.118138, 2020.

42. Paulot, F., Paynter, D., Ginoux, P., Naik, V., Whitburn, S., Van Damme, M., Clarisse, L., Coheur, P. F., and Horowitz, L. W.: Gas-aerosol partitioning of ammonia in biomass burning plumes: Implications for the interpretation of spaceborne observations of ammonia and the radiative forcing of ammonium nitrate, 44, 8084-8093, https://doi.org/10.1002/2017GL074215, 2017.

43. Pant, P., and Harrison, R. M.(2013): Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review, Atmos. Environ., 77, 78-97, https://doi.org/10.1016/j.atmosenv.2013.04.028.

44. Pant, P., and Harrison, R. M.(2012): Critical review of receptor modelling for particulate matter: a case study of India, Atmos. Environ., 49, 1-12.

45. Grigoratos, T., and Martini, G (2019): Brake wear particle emissions: a review, Environ. Sci. Pollut. Res., 22, 2491-2504, 10.1007/s11356-014-3696-8, 2015.

46. Piscitello, A., Bianco, C., Casasso, A., and Sethi, R.: Non-exhaust traffic emissions: Sources, characterization, and mitigation measures, Sci. Total Environ., 766, 144440, https://doi.org/10.1016/j.scitotenv.2020.144440, 2021.

47. Smichowski, P., Gómez, D., Frazzoli, C., and Caroli, S.: Traffic-Related Elements in Airborne Particulate Matter, Applied Spectroscopy Reviews, 43, 23-49, 10.1080/05704920701645886, 2007.

48. Duong, T. T. T., and Lee, B.-K.: Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics, J. Environ. Manage., 92, 554-562, https://doi.org/10.1016/j.jenvman.2010.09.010, 2011.

49. Liao, H.T., Chou, C.C.K., Chow, J.C., Watson, J.G., Hopke, P.K., Wu, C.F., (2015). Source and risk apportionment of selectes VOCs and PM2.5 species using partially constrained receptor models with multiple time resolution data. Environ. Pollut. 205, 121-130.

50. Yu, L., Wang, G., Zhang, R., Zhang, L., Song, Y., Wu, B., Li, X., An, K., and Chu, J. (2013): Characterization and source apportionment of PM2.5 in an urban environment in Beijing, Aerosol Air Qual. Res., 13, 574-583, 10.4209/aaqr.2012.07.0192.

51. Zhang, Y., Sun, J., Zhang, X., Shen, X., Wang, T., and Qin, M. (2013): Seasonal characterization of components and size distributions for submicron aerosols in Beijing, Sci. China Earth Sci., 56, 890- 900, 10.1007/s11430-012-4515-z.

52. Paul M Lemieux, Christopher C Lutes, Dawn A Santoianni (2004): Emissions of organic air toxics from open burning: a comprehensive review, Progress in Energy and Combustion Science, 30, 1, https://doi.org/10.1016/j.pecs.2003.08.001

53. Available at the link: https://www.undp.org/north-macedonia/blog/scaling-solutions-leveraging-open-data-tackle-air-pollution

54. Available at the link: https://environment.ec.europa.eu/topics/urban-environment/inspiration/krakow-air-protection_en

55. Guidelines for drafting air quality improvement plan. http://air.moepp.gov.mk/wp-content/uploads/2017/04/Pravilnik-plan-za-podobruvanje-na-kvalitetot-na-vozduhot.pdf