

Proceeding Paper

Source Apportionment of the Atmospheric Aerosol in Western Macedonia, GREECE, Part 1: Concentrations of Metallic Components, Major Ions, and PAHs in PM₁₀ Samples [†]

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Abstract: The government decision to promote the change of energy mix has led to a serious decrease in industrial activities in the energy basin of Western Macedonia and subsequently had a positive influence on the air quality of the region. To examine the fact and estimate the current atmospheric emission sources, PM₁₀ samples were collected at different sites in Western Macedonia, Greece, from February 2022 to May 2023 and were analyzed for metallic components, major ions, and PAHs. The dataset was then analyzed using PMF and CMB model to identify the possible emission sources. In this study, the first results are presented and discussed.

Keywords: PM₁₀; metallic components; PAHs



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1. Introduction

One of the most significant pollutants aggravating air quality and impacting human health is ambient particulate matter and especially the inhalable fraction (PM₁₀).

Generally, suspended particles are emitted from various sources (such as soil dust, marine aerosol, natural forest fires, volcanic activity, industrial emissions, transportation, wood burning, fossil fuel consumption, etc.) as a primary or secondary pollutant while they consist of organic and inorganic fraction [1]. Among their prevailing chemical constituents are associated metal(oid)s, particle-bound polycyclic aromatic hydrocarbons, and ionic species.

In order to identify emission sources and evaluate their contribution on ambient PM fraction, it is functional to qualify the chemical composition of atmospheric PM mass. Among the various assessment techniques, receptor modelling is a source-apportionment methodology that is widely applied to different areas affected by miscellaneous emission sources using pollutant concentration levels and meteorological data taken at receptor sites.

Up to today, a limited number of source-apportionment studies for the area of Western Macedonia have been published using receptor models. Moreover, all these studies only concern residential sites related to the lignite energy basin [2–5].

The objective of the current work is to determine the ambient PM₁₀ concentrations levels at different sites in Western Macedonia and find out their chemical components regarding associated elements, particle-bound polycyclic aromatic hydrocarbons, and ionic

species. In the present study, some first results of particulate matter chemical analyses are presented and described.

It must be noted that the present study represents the first part of a wider project which aims to spot dust-emission sources and explore their influence on receptors as the delignification proceeds rapidly. For this purpose, four sites were selected based on the dominant emission sources impacting the sampling sites (urban, traffic, industrial, trans-boundary pollution, and background pollution). Finally, the datasets of PM concentration levels and their chemical constituents presented here will be used in a second stage to assist source-apportionment studies through receptor modeling.

2. Monitoring

2.1. Study Area

Four receptor sites (Figure 1) were chosen based on the prevailing emission sources.

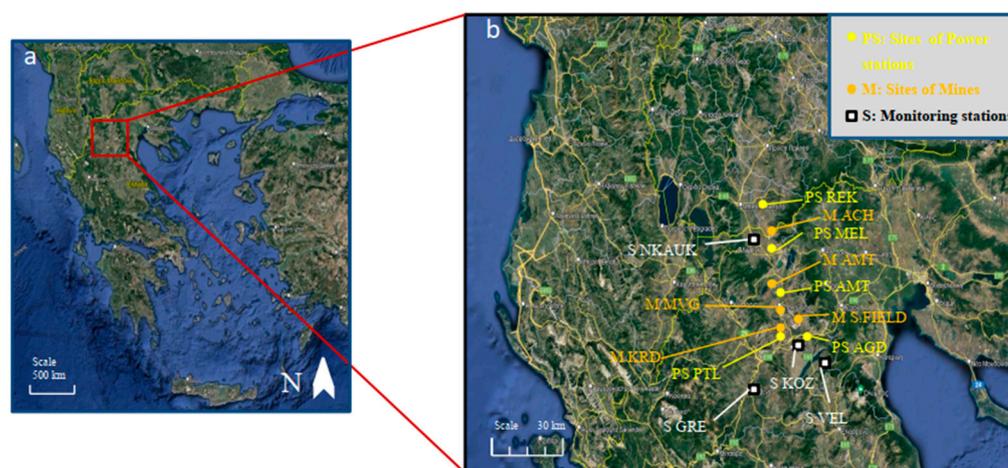


Figure 1. (a) Study area—NW Greece. (b) Map showing the receptor sites (S). The lignite power stations (PS, only two of these are in operation, AGD—Greece and REK Bitola—North Macedonia) and the opencast lignite mines in Western Macedonia, Greece, are also shown.

The first sampling site is located within the built environment in the city of Kozani (SKOZ, 40.299° N, 21.799° E, 711 m above sea level, 50,000 inhabitants), where urban activities take place, and anthropogenic emissions are dominant.

The second site is in Grevena city (SGRE, 40.082° N, 21.426° E, 526 m asl, 16,500 inhabitants) where biomass (wood and its derivatives) and oil consumption are the major energy sources for residential use. Urban activities and traffic also occur.

The third is in Neos Kaukasos (SNKAUK, 40.894° N, 21.472° E and 594 m asl), a hamlet with 230 inhabitants in a rural district, which is affected by industrial transboundary pollution. It is located 500 m away from the Greek–North Macedonian borders and about 15 km from the coal mines and lignite Power Plant (REK Bitola).

The fourth is in an area mainly covered by tree crops where farming activities (use of pesticides, ploughing etc.) generally take place. Specifically, it is located at west northwest sector of the village Velvendos and about 200 m away from the settlement (SVEL, 40.259° N, 22.064° E and 385 m asl, 3400 inhabitants). So, this receptor can be considered as rural.

2.2. Ambient Sampling

A one-year sampling of airborne particulate matter (PM₁₀) was conducted at four chosen receptors in Western Macedonia, Greece, from February 2022 to May 2023. The 24 h samples of suspended particles were collected by filtration on PTFE membrane filters (teflo, Pall) using low-volume (2.3 m³ h^{−1}) air samplers (PM162M Environment S.A. and Derenda LVS). Unloaded and loaded filters placed on open but dust-protected sieve trays, were exposed before and after sampling for 48 h to steady temperature and relative humidity

($T = 22 \pm 2$ °C and R.H. = $43 \pm 5\%$) in an air-conditioned weighing room. The determination of particle mass concentrations was carried out gravimetrically using an analytical microbalance, placed in the weighing room while the static electricity from the filters and tools used was eliminated by a static eliminator. Overall, 64, 90, 75 and 89 samples were selected for each site SKOZ, SGRE, SNKAUK and SVEL, respectively.

2.3. Elemental Analysis

The chosen filters (7, 31, 8 and 10 samples for SKOZ, SGRE, SNKAUK and SVEL, respectively) regarding the period from February to August 2022 were digested by an Anton Paar Multiwave GO Plus microwave digestion system (Method 3051A) using 6 mL mixed acid (3:1 high purity HNO_3 and HCl). The extracts were filtered through syringe filter (PTFE, 0.45 μm pore size) and diluted to 25 mL with high-purity water. Eventually, the final aqueous solutions were analyzed by ICP-MS (Agilent 7500) for the determination of Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Cu, As, Se, Mo, Ag, Cd, Sb, Ba, Pb, Th and U. The elemental concentrations were corrected using blank samples and taking into account the recovery rates for each chemical component.

2.4. Extraction and PAH Analysis

The representative number of samples was analyzed to determine the PM10-bound PAHs. The organic fraction was obtained from the filters using the two-stage extraction method. Initially, PTFE membrane filters were extracted via refluxing with 5 mL hexane for 30 min. The second stage was carried out using an ultrasonic extraction technique by 5 mL hexane–acetone mixture (1/1) for 15 min. The two-stage extracts obtained were transferred in 10 mL vials and were finally concentrated up to 0.1 mL under the gentle pure-nitrogen gas flow.

The final extracts were analyzed for PAHs by Agilent Technologies 6890 N gas chromatograph coupled to a 5973-mass selective detector (GC-MSD) operated in the selected ion-monitoring mode (SIM).

2.5. Extraction and Analysis of Ionic Species

The third quarter of the filter was treated in an ultrasonic bath for 30 min with 10 mL of ultra-pure water (Millipore Direct Q, resistivity 18.2 M Ω). The extracts after filtration through 0.45 μm Nylon syringe filters were injected to a Metrohm 850 Professional, chromatographic system. The ion chromatography injection volume was 20 μL , the run time was 30 min, and the column temperature was kept to 30 °C. Field and laboratory blanks were routinely analyzed for ionic species and the results were subtracted from the sample values.

3. Results and Discussion

3.1. PM10 Concentrations

The measurement campaign was conducted throughout a year at four receptor sites SKOZ (April 2022 to May 2023, $n = 64$), SGRE (February 2022 to May 2023, $n = 90$), SNKAUK (Jun 2022–May 2023, $n = 75$) and SVEL (April 2022 to May 2023, $n = 89$), and the PM10 concentrations were determined gravimetrically. The mean annual concentrations of PM10 during the sampling period at the four receptors are presented in Table 1. As seen, the average concentrations of PM10 in all cases were below the EU-proposed annual limit value of 40 $\mu\text{g m}^{-3}$ (83/399/ECC) [6].

The highest PM10 values were recorded at Kozani and Grevena, where urban activities take place, and anthropogenic emissions are generally dominant. The mean values of PM10 levels were 18 and 25 $\mu\text{g m}^{-3}$, and the daily concentrations were ranging from 5 to 64 and 5 to 57 $\mu\text{g m}^{-3}$, respectively.

In accordance with the directive 2008/50/EC [7], the 24 h limit value of 50 $\mu\text{g m}^{-3}$ for PM10 has been exceeded once (1.6%) in the case of Kozani and three times (3.3%) at the

measuring station of Grevena. However, no value recorded on a 24 h basis exceeded the daily limit at the SNKAUK and SVEL stations.

Table 1. Statistical data of PM10 concentration level analysis.

| Receptors | n | Sampling Period | Average [$\mu\text{g m}^3$] (min–max) | Exceedances No (%) |
|-----------|----|--------------------|--|--------------------|
| SKOZ | 64 | April 22–May 23 | 18 (5–64) | 1 (1.6%) |
| SGRE | 90 | February 22–May 23 | 25 (5–57) | 3 (3.3%) |
| SNKAUK | 75 | June 22–May 23 | 17 (4–45) | - |
| SVEL | 89 | April 22–May 23 | 14 (4–36) | - |

3.2. Elemental Concentrations

Restricted number of ambient PM10 samples regarding the period from February to August 2022, after collection and weighing, underwent a chemical analysis to determine the associated metals and metalloids at the receptors. Specifically, 7, 31, 8 and 10 filters were chosen and analyzed from SKOZ, SGRE, SNKAUK and SVEL, respectively. For the selection of sampling filters, the prevailing meteorological conditions, and the PM10 concentration levels were taken into account.

The first results of PM10 chemical analyses are shown in Table 2 where the elemental composition of particle matter at the sampling sites is summarized. Through examining these records, a wealth of information is drawn regarding specific properties and characteristics of collected aerosols such as their origin, toxicity, etc.

Table 2. Particle mass and associated elemental components—first results of chemical analysis.

| | | SKOZ (n = 7) | | SGRE (n = 31) | | SNKAUK (n = 8) | | SVEL (n = 10) | |
|------|-------------------|--------------|------|---------------|------|----------------|------|---------------|------|
| | | Average | SD | Average | SD | Average | SD | Average | SD |
| PM10 | $\mu\text{g m}^3$ | 22 | 7 | 29 | 12 | 18 | 4 | 19 | 7 |
| Be | ng m^3 | 0.03 | 0.02 | 0.02 | 0.03 | 0.02 | 0.01 | 0.02 | 0.01 |
| Na | ng m^3 | 89 | 113 | 142 | 201 | 115 | 82 | 111 | 122 |
| Mg | ng m^3 | 215 | 137 | 211 | 223 | 126 | 49 | 133 | 79 |
| Al | ng m^3 | 203 | 173 | 178 | 236 | 181 | 82 | 147 | 145 |
| K | ng m^3 | 184 | 160 | 496 | 394 | 172 | 94 | 213 | 117 |
| Ca | ng m^3 | 1556 | 587 | 998 | 787 | 519 | 423 | 859 | 547 |
| V | ng m^3 | 1.4 | 0.9 | 1.2 | 1.2 | 1.2 | 0.4 | 0.9 | 0.4 |
| Cr | ng m^3 | 2.9 | 1.5 | 3.4 | 1.6 | 1.5 | 0.7 | 3.1 | 1.4 |
| Mn | ng m^3 | 12 | 9 | 10 | 9 | 10 | 4 | 8 | 5 |
| Fe | ng m^3 | 579 | 404 | 477 | 495 | 433 | 169 | 340 | 211 |
| Co | ng m^3 | 0.3 | 0.2 | 0.33 | 0.25 | 0.3 | 0.2 | 0.19 | 0.10 |
| Cu | ng m^3 | 5 | 2 | 5 | 4 | 3 | 5 | 3 | 2 |
| As | ng m^3 | 0.6 | 0.4 | 0.40 | 0.20 | 0.7 | 0.4 | 0.3 | 0.2 |
| Se | ng m^3 | 0.5 | 0.2 | 0.42 | 0.17 | 0.4 | 0.1 | 0.5 | 0.2 |
| Mo | ng m^3 | 0.09 | 0.08 | 0.04 | 0.04 | 0.07 | 0.09 | 0.1 | 0.3 |
| Ag | ng m^3 | 0.04 | 0.03 | 0.04 | 0.05 | 0.02 | 0.02 | 0.1 | 0.2 |
| Cd | ng m^3 | 0.2 | 0.1 | 0.24 | 0.20 | 0.2 | 0.2 | 0.1 | 0.1 |
| Sb | ng m^3 | 0.4 | 0.1 | 0.31 | 0.15 | 0.2 | 0.2 | 0.2 | 0.1 |
| Ba | ng m^3 | 5 | 3 | 5 | 5 | 3 | 2 | 5 | 6 |
| Pb | ng m^3 | 4 | 9 | 16 | 39 | 32 | 72 | 7 | 15 |
| Th | ng m^3 | 0.11 | 0.08 | 0.08 | 0.11 | 0.11 | 0.06 | 0.07 | 0.04 |
| U | ng m^3 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 |

More specifically, the total mass of the chemical species determined as a percentage of the PM10 mass was 12.96, 8.75, 8.86 and 9.61% for SKOZ, SGRE, SNKAUK and SVEL receptor sites, respectively. As it seems, the crustal elements (Al, Ca, Mg, and Fe) were the

most abundant components contributing to PM₁₀ mass, indicating that the earth surface constitutes a significant emission source.

At all sites, mean Pb values were well below the ambient air quality standard of 500 ng m⁻³ (as annual mean, EC, 1999) [6]. Moreover, as it turns out, the mean concentrations of As and Cd were also lower than the proposed assessment thresholds (6 and 5 ng m⁻³, respectively, EC, 2003). In the case of V, the proposed 24 h concentration is 1 µg m³, a value never exceeded during the sampling campaign (WHO, 2000) [8]. Finally, the mean total concentration of Mn was found lower than the annual tolerance concentration included in the WHO Air Quality Guidelines (150 ng m⁻³, WHO, 2000) [8].

The above-mentioned results and observations constitute a small part of data to draw safe conclusions through receptor modeling.

So, with a view to estimate the contribution of PM emission sources on atmospheric PM mass and investigate this problem in depth, it is of great importance to gather as many data as possible regarding the chemical composition of PM₁₀ samples.

Bearing that in mind, it is considered necessary to continue the chemical analyses of collected ambient dust samples.

4. Conclusions

1. The PM₁₀ measurement campaign was conducted throughout a one-year period at three receptor sites with different features in Western Macedonia, a region in NW Greece with mining and lignite power activities.
2. The mean PM₁₀ values from all the sampling sites were below the annual limit value of 40 µg m⁻³.
3. The 24 h limit value of 50 µg m⁻³ for PM₁₀ has been exceeded once (1.6%) in the case of Kozani and three times (3.3%) at the measuring station of Grevena. No value recorded on a 24 h basis exceeded the daily limit at the New Kaukasos and Velvento stations.
4. Crustal matter (such as oxides of Al, Ca, Mg, and Fe) made up the main components of PM₁₀.
5. At all receptor sites, the mean values of Pb, V, As, and Cd were lower than the proposed assessment thresholds.

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