Alda Kika¹, Alma Shehu², Sonila Kane Shehu², Pranvera Lazo²*

¹University of Tirana, Faculty of Natural Sciences, Department of Computer Sciences, Tirana, Albania, ²University of Tirana, Faculty of Natural Sciences, Department of Chemistry, Tirana, Albania



Zastita Materijala 64 (4) 402 - 412 (2023)

A preliminary study on assessment of air quality in Tirana, Albania

ABSTRACT

The concentrations of particulate matter and Fe in airborne particulate matter and transplanted moss were investigated to evaluate the air quality of Tirana city. It was carried out in the summer of 2021 and the winter of 2020-2021. Particulate matter of various sizes (PM2.5 and PM10) was collected on Teflon-coated glass fibre filters. Fe was determined in PMs and moss transplants, the last were exposed for two months at the same monitoring site as PMs. The measurements were carried out in areas with heavy traffic during the summer under relatively high air temperatures, up to 23° C, which can affect the high concentrations of solid particles in the air and therefore high Fe levels. Statistical analysis was used to discuss the results of particulate matter and iron in solid particles and moss. A higher concentration of Fe was found in total suspended particles (TSP) and a lower concentration in smaller particles. The concentration data were compared with the recommended values in the European Directives. The concentrations of all parameters under investigation were higher than the permitted ones for rural and residential areas and lower than the recommended values for industrial areas. Correlation analysis revealed high and significant correlations (R > 0.8, p < 0.05) between Fe concentrations in moss transplants and particulate matter, showing a high effect of particulate matter on airborne Fe. It may increase human exposure through inhalation and lead to harmful health problems. This requires stronger measures to improve air quality in the city.

Keywords: air quality, PM, moss bags, cross roads, residential area, Tirana

1. INTRODUCTION

Environmental pollution has been a crucial global concern in recent decades, both regarding the survival of the living world and the use of biological assets in the country, in addition to human health. Airborne particulate matter (PM), a constituent of Earth's atmosphere [1], is considered a big threat to our world [2]. PMs less than 10 µm (PM10, PM2.5, etc.) consist of a complex composition of both organic and inorganic compounds and toxic metals [2-4], which arise from both natural and anthropogenic sources [1,2,5]. The presence of high levels of PM in residential areas is mostly affected by residential heating, industry, traffic emissions, and the construction industry. Among them, vehicular traffic, industry, and fuel-burning activities are important sources of

particulate matter (PM) and trace metals in the atmosphere. In many European countries. industrial and municipal emissions have been significantly reduced during the last three decades; therefore, vehicular emissions have become the most critical source of urban air pollution [6]. It contains trace amounts of toxic metals coming from the abrasion and corrosion of metal parts of the engine and from the exhaust and non-exhaust emissions, e.g., from the wearing of tires, brakes, and other parts of vehicles [6]. The physical and chemical properties of anthropogenic PM have a detrimental effect on human health and natural processes [1].

Traditional monitoring is a high-cost and timeconsuming method, so an alternative method of biomonitoring that employs biological species as biomonitors is widely used in Europe [7,8]. It is a low-cost method that provides а aood representation of the spatial distribution, relative pollution levels at local and regional scales, and temporal variations in the pollution level [9]. Mosses and lichens have been used as biomonitors in atmospheric deposits of trace metals, radionuclides, and organic compounds

^{*}Corresponding author: Pranvera Lazo

E-mail: pranveralazo@gmail.com

Paper received: 30. 04. 2023.

Paper accepted: 19. 07. 2023.

Paper is available on the website: www.idk.org.rs/journal

[7,8,10-14] passive for and/or active biomonitoring. Active biomonitoring, or the sotechnique", called "moss bag uses moss transplants packed in small bags. It has been widely used in urban areas because terrestrial mosses are absent due to the high level of air pollution from anthropogenic activity in the area [15]. Active biomonitoring of trace metals in various urban and industrial (micro) environments is a simple and easily applicable technique in any experimental design that represents a timeintegrated response to persistent air pollutants on a certain scale over several months [15-19], urban [20-22], and agricultural [15,23] areas.

Air pollution is a main environmental concern in major Albanian cities, particularly in Tirana. It is mostly coming from old diesel vehicles that remain problematic. Other sources of air pollution include coal and wood burning for heating, industrial emissions, waste incineration, agricultural and construction activities, and diesel generators, which are the main sources of fine solid particles (PM2.5 and PM10), ozone, nitrogen oxides, sulfur dioxide, carbon dioxide, and toxic metals in the air, responsible for premature deaths each year. Data on air quality are scarce because monitoring at the national level is neither comprehensive nor permanent. The air quality index (AQI) data published by the 2021 World Air Quality Report [24], which analyzes PM2.5 data reported by ground-level monitoring stations around the world, show that the AQI in Tirana exceeds the 2021 annual guideline level for PM2.5 of 5 µg/m³. Due to the severe impact of air pollution on global health, the recommended level for the 2021 PM2.5 annual guideline was dropped from the previous 10 μ g/m³ decided by the 2005 guideline level to 5 n/m³ [24].

This research aimed to investigate the air quality in Tirana, Albania, by measuring airborne particulate matter (TSS, PM10, and PM2.5) and iron mass concentrations included in airborne particulate matter and transplanted moss, which were exposed for two months along five sampling sites. The origin of Fe in the air comes from both natural and anthropogenic sources. Concentrations of Fe in the atmosphere of different cities vary in a wide range, from 0.130 to 14 μ g/m³, and are extremely elevated in the air of urban regions compared to their contents in the air of rural regions [25].

2. MATERIAL AND METHODS

2.1. Study Area

Tirana, with a surface area of only 42 sq. km, is located at 41°19'48" N and 19°49'12" E and has an average altitude of about 110 m. Tirana is surrounded by Dajti Mountain in the east, with the highest altitude of 1828 m, a small valley in the northwest, and hills on the rest of the sites. Tirana has a classic Mediterranean climate with hot and dry summers and cool and rainy winters, and an average temperature of 15°C. The annual rainfall is about 1265 mm, with low precipitation during the summer and high precipitation during the winter.

The city of Tirana was growing very fast, from 250 thousand in 1989 to 850 thousand in 2018. It was followed by an increase in traffic volumes, which has caused environmental challenges concerning traffic congestion and air pollution. There are about 201,000 cars per day in use in Tirana, which has an area of about 31 km² and a population of less than one million inhabitants. Old diesel-engine vehicles remain a big source of air pollution.

2.2. Sampling

Daily monitoring was conducted in Tirana city as a preliminary study for assessing air quality due to dust and inhaling particles (PM10 and PM2.5). Ambient air sampling was carried out during May– June 2021, in the morning, midday, and afternoon. Sampling time was set aside during busy traffic periods (8 a.m., 9 a.m., and 10 a.m.; 1 p.m., 2 p.m., and 3 p.m.; and 6 p.m., 7 p.m., and 8 p.m.). The MCZ Micro PNS/LVS-1 instrument, equipped with a small volume air sampling pump, with a flow rate of 38.5 L/min, was used for sampling TSP, PM10, and PM2.5 samples. Air samples were collected by pumping air into the filter for 4 hours.

The sampling device was equipped with three cyclone sampling heads and Teflon filters to support the collection of different air particle sizes. Samplings were performed following the procedure recommended by European legislation (UNI EN-12341:2014) [26]. High-purity quartz filter papers (Whatman grade, 47 mm), dried to a constant weight for about 48 hours and then packed and stored in Petri dishes, were used for sampling. Filters were stored in a cool and dark place untill the next step of analysis (at most for one day). Monitoring sites were elected in heavy traffic and residential areas, the last was used as a reference point.

Each sampling area was free of obstructions that may affect the airflow in the vicinity of the sampler, such as trees, balconies, walls, etc. Sampling instruments were kept at an elevation of 1.7 m above ground level and at least 0.5 m from the nearest building, following the standard monitoring guideline, SIST EN 12341:2014 [26]. The initial and final weights of filter papers were taken using a Sartorius (CPA225D, ±0.01 mg) balance. The differences were recorded to TSP, calculate PM10. and PM2.5 mass concentrations. To minimize the error due to filter handling, field blank filters and lab blanks were used. The collected samples were kept in polyethylene bags and stored at 4° C in a refrigerator. The air PM content was calculated by the following equations:

$$PM(\mu g/m^3) = \frac{w_2 - w_1}{Q * T} \times 10^6$$

and:

$$Fe(\mu g/m^3) = \frac{Fe(\mu g/filter)}{Q*T} \times 10^6$$

where:

 W_1 = weight before sampling (g);

 W_2 = weight after sampling (g); Q = flow rate (38.5 l/min = 2.31 m³/h); t = sampling time (9 h); Fe (in µg) = Fe content in PM

Filters containing the PMs were digested with aqua regia (HCI: $HNO_3 = 3:1$) and diluted for further determination of Fe concentration by using the graphite furnace atomic absorption spectrometer (GFAAS). Figure 1 shows the position of sampling sites in the study area and Table 1 shows the geographic coordinates of each sampling site.

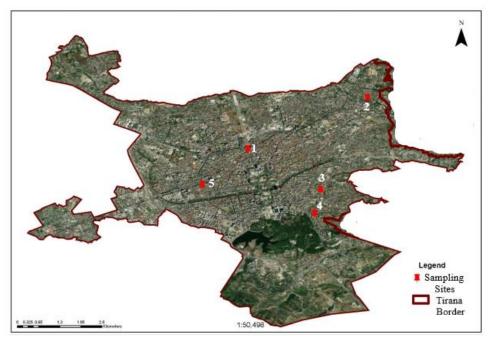


Figure 1. GIS map of Tirana with the position of sampling sites in the study area Slika 1. GIS karta Tirane sa pozicijom lokacija za uzorkovanje u oblasti istraživanja

- Table 1. Coordinate data for each monitoring site (dry precipitation, t = 21 to $24^{\circ}C$)
- Tabela 1. Koordinatni podaci za svako mesto praćenja (suve padavine, $t = 21 \text{ do } 24^{\circ}C$)

Sites	Longitude	Latitude
S1	41.33451	19.81631
S2	41.33994	19.84966
S3	41.31755	19.83535
S4	41.30525	19.83787
S5	41.32518	19.80327

Hypnum cupressiforme Hedw, moss species collected at a national park free from anthropogenic pollution sources in Belgrade, Serbia, was used for this study. The upper green parts of the moss after cleaning from extraneous materials, washed three times with bi-distilled water and air-dried, were used to prepare the moss bags [27]. About 5 g moss was packed in polyethylene nets, hanged at 3 m above ground level, and exposed at each site for two months [21], were. The geographic elevations of the sampling sites are 110 m.

Moss bags were exposed in triplicate in the open spaces of five sites for two months during the winter (from December 1, 2019 to February 1, 2020). To keep the moss samples stable until the chemical analysis, they were dried at 40 °C for 24 hours under clean lab conditions [16,17,21,27-33].

2.3. PM assessment and Fe chemical analysis

The TSP, PM10, and PM2.5 masses were calculated as the difference in dried filter mass weighted before and after sampling. The concentration of TSP, PM10, and PM2.5 (m/V) is

calculated by dividing the mass of PMs trapped in the filter by the volume of air passed during the sampling time. The result is expressed in μ g/m3 at standard conditions of temperature (273 °K) and pressure (101.3 kPa, 760 mm Hg). Fe concentration in air particles was measured by a graphite furnace atomic absorber spectrometer (Analytik Jena novAA 400).

Around 0.5 g of moss was digested in halfpressure Teflon digestion vessels. The vessels were placed on the hotplate for two hours at 250° C after adding 9 ml of HNO₃ (69%, m/V, Merck, Germany) and 1 ml of ml H₂O₂ (30%, m/V, Merck, Germany). The digested solutions were quantitatively transferred into 50 ml calibrated flasks. Analytical yield (recovery, R%) was also calculated using the standard addition method. Blank samples and replicates were analyzed in parallel with PM and moss samples.

2.4. Data analysis

The Anderson-Darling test, confirmed at p > 0.05 was used to check the normality distribution of the data, as well as the lognormal distribution probability plot confirmed at the same p level. To bring the Fe data into the same digit number, the standardized moss data were calculated as the ratio of Fe concentration in moss exposed at each monitoring site to the minimum value of Fe under the same conditions. The pollution level is evaluated by the pollution index (PI), calculated as the ratio between the concentration of each parameter and the corresponding value at the control site [34].

 $PI = C_i/S_i$

Ci - concentration of parameter i;

Si - concentration of parameter i in control site.

Pollution level is established as [34]:

- PI ≤ 0.7, clean
- $0.7 < PI \le 1.0$, no-contaminated
- $1.0 < PI \le 2.0$, slight pollution
- $2.0 < PI \le 3.0$, moderate pollution
- $PI \ge 3.0$, serious/very high pollution

The relationship between the measured parameters was checked by Pearson correlation classified as "very strong" (r > 0.8), "strong" (r = 0.6-0.8), or "moderate" (r = 0.4-0.6) correlations. Cluster analysis (CA) was used to investigate the sources of contaminants in air pollutants. CA is a multivariate method used for differentiating the data into clusters based on their similarity levels [35]. The hierarchical cluster method, which differentiates the data into different clusters with a multi-level hierarchy based on the distance between observations in the data set and their similarity [36], was applied. It made possible the visualization of clusters that present a picture of the groups and their proximity with a distinct reduction in the dimensionality of the original data [35]. The statistical data analysis was performed using the MINTAB 21 software package.

3. RESULTS AND DISCUSSION

The assessment of air quality was carried out through the study of the levels and distributions of the content of PM, TSP, and Fe in PM and moss exposed at the same position as PM. The assessment is based on the recommended values regarding the content of metals in the air. The results obtained for the concentration of PMs, TSP, and Fe in solid fine particles and the exposed moss are shown in Table 2.

Table 2. Concentration of PMs and Fe in each monitoring site (* $\mu g/m^3$, mg/kg in moss)

Site	TSP*	PM10*	PM2.5*	Fe _{TSP*}	Fe _{PM10}	Fe _{PM2.5*}	Fe _{moss*}	Fe _{moss(ST)}	PM10/PM2.5
S1	303	260	47	8.4	4.21	1.9	827	1.33	5.53
S2	66	47	22	7.85	3.78	1.64	622	1.0	2.14
S3	150	112	37	8.25	4.07	2.02	717	1.15	3.03
S4	500	405	76	8.8	4.73	2.3	1129	1.82	5.33
S5	439	388	55	8.49	4.4	1.91	926	1.49	7.05

The concentration data of TSP, PM10, and PM2.5 showed moderate variations (CV% ranged from 25% to 75%), while Fe measured in PMs of different sizes and moss samples showed very low variation (CV% < 25%). TSP, PM10, and PM2.5 varied from 66 μ g/m³ to 500 μ g/m³ (TSP), 67 μ g/m³ to 405 μ g/m³ (PM10), and 22 to 46 μ g/m³ (PM2.5).

It means the data were relatively stable during the monitoring times and were affected by various factors. The concentration of Fe in TSP varies from 2.6–8.8 μ g/m³, with an average value of 7.04 μ g/m³ and a standard deviation of 2.5 μ g/m³. Distribution of Fe in TSP, based on the value of P = 0.015 < 0.05. It indicates the data did not follow normal

distributions and were affected by various factors. The data for PM10 and PM2.5 show low variability and follow normal distributions (p > 0.05, tested by

the Anderson-Darling test). It means the data were stable during the monitoring.

Table 3. Descriptive Statistics data of PMs and Fe in PM and moss bag samples (in $\mu g/m^3$; ¹ in mg/kg)

Tabela 3. Podaci deskriptivne statistike o PM i Fe u uzorcima PM i vreća od mahovine (u μg/m3; 1 u mg/kg)

Variable	N	Mean	StDev	CV%	Min	Median	Max
TSP	5	292	185	63	66	303	500
PM10	5	242	161	66	47	260	405
PM2.5	5	47	20.2	43	22	47	76
FeTSP	5	8.4	0.348	4	7.85	8.4	8.8
Fe _{PM10}	5	4.2	0.356	8	3.78	4.21	4.7
Fe _{PM2.5}	5	2.0	0.238	12	1.64	1.91	2.3
Fe _{moss}	5	844	196	23	622	827	1129
Fe _{moss(ST)}	5	1.36	0.315	23	1.00	1.33	1.82

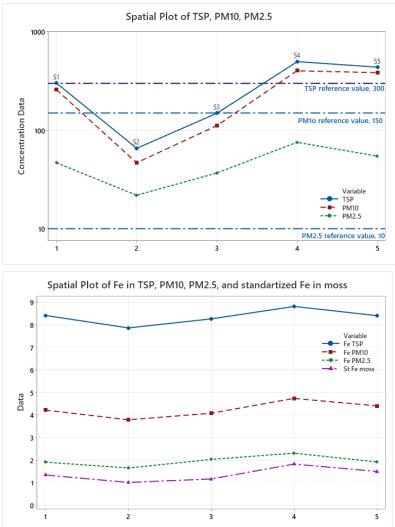
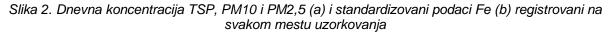


Figure 2. Diurnal TSP, PM10, and PM2.5 concentration (a) and Fe standardized data (b) registered at each sampling site



The diurnal levels of TSP, PM10, PM2.5, and Fe in each fraction of particulate matter and moss at all sampling sites are presented in Figs. 2a and b. It can be seen that the residential site (S2) showed the lowest concentrations of each parameter, followed by the next residential site, S3. The highest particulate matter and Fe concentrations were found at S4, a site positioned next to the highway, followed by heavy traffic crossroad sites (S4 and S1). The estimated concentrations of particulate matter show moderate variability in the city among monitoring sites. The diurnal TSP and PM10 concentrations of S1, 4, and 5 were found to be very high, higher than the reference values decided by the EU guideline for short-term exposure over 24 hours [39], while lower concentrations, lower than the same EU guideline, were found at both residential sites S2 and S3.

The airborne PM2.5 concentration, the most dangerous PM fraction, was estimated at a high level, higher than the EU guideline value [39]. It ranged from 22 μ g/m³ to 76 μ g/m³, with the highest concentrations at heavy traffic sites (S1, S4, and S5), and lower concentrations in residential sites (S2 and S3). PM2.5 followed the same spatial trend as TSP and PM10. The concentration of PM2.5 at all sampling sites, except residential site

S2, exceeds the first interim target from the World Health Organization, 35 μ g/m³ [40]. PM2.5 is a global problem, as it has the largest health impact because more than half of the global population is exposed to annual-average ambient concentrations exceeding the first interim target from the World Health Organization, 35 μ g/m³ [40].

The PM10/PM2.5 ratio varied from 2.14 at S2, a residential site, to 7.05 at S5, a heavy-traffic site. High PM10/PM2.5 ratios are formed from coarse particle emissions in the form of soil dust particles and re-suspended road dust present in PM10, fresh combustion emissions in residential sites, combustion and traffic emissions (motor vehicles, open burning, and oil), and secondary species (NO₃⁻, SO₄²⁻ and NH₄⁺), all present in the PM2.5 fine fraction [41-44]. Fe, a crustal element, was found at high concentration levels in all sites. The highest concentrations of Fe were found at S4 and S5 heavy traffic sites, probably as a result of dust emissions from re-suspended road dust. All these indicate that major sources of PM10 were geogenic materials like soil dust, re-suspended road dust, and traffic emissions, while PM2.5 could be caused by vehicle emissions and secondary species mostly from anthropogenic sources [41].

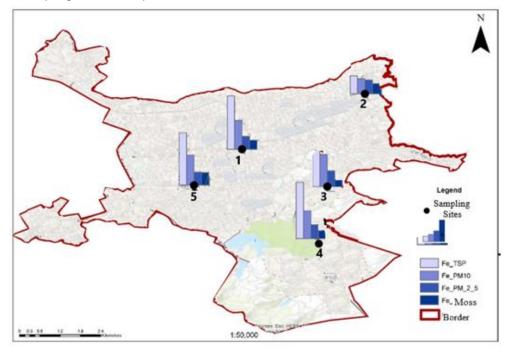


Figure 3. Fe distribution along sampling sites Slika 3. Raspodela Fe duž mesta uzorkovanja

The differences between TSP, PM10, and PM2.5 average concentrations in heavy traffic sites and residential sites were very high: $306 \ \mu g/m^3$, $272 \ \mu g/m^3$, and $30 \ \mu g/m^3$ respectively. This indicates a high level of traffic and re-suspended

road dust in Tirana city. To explain these differences and estimate urban air quality, it is necessary to evaluate the city's emissions inventories. The largest contributors to particulate matter concentrations (TSP, PM10 and PM2.5) in

Tirana are the construction industry, traffic emission, soil dust emissions, residential and commercial activities, and urban waste management. As proposed by Pastuszka et al. (2010) [6], the relative increment (RI) of particulate matter concentration at crossroads was estimated as the ratio of the difference between the concentration of PM at a certain site (C_i) and the lowest PM concentration at the rural site, here the residential site, considered as background concentration (C_{BC}) to C_{BC}

$$RI\% = 100(C_i - C_{BC})/Average(C_i)$$

Table 4 The relative increment (RI%) of particulate matter and Fe concentration near the crossroads

Site	TSP%	PM10%	PM2.5%	(Fe TSP)%	(Fe PM10)%	(Fe PM2.5)%	(Fe moss)%	(St Fe moss)%
S1	81	88	53	7	10	13	24	24
S2	0	0	0	0	0	0	0	0
S 3	29	27	32	5	7	19	11	11
S4	149	148	114	11	22	34	60	60
S5	128	141	70	6	15	14	36	36

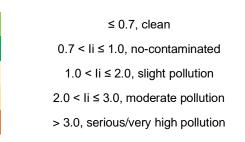
The RI% values ranged from 29% to 149%, with an average value for TSP, 27% to 148% for PM10, and 32% to 114% for PM2.5. It shows that the effects of traffic emissions on PM10 and PM2.5 concentration levels at the crossroads of Tirana are very high. It is expected, if we consider the number of cars, mostly old cars, being used, to be about 201,000 cars per day in an area of 31 km² and a population of 863,694 inhabitants of Tirana city.

Pollution levels are evaluated based on the pollution index (PI) [34]. The PI data show serious pollution from TSP and PM10 at sampling sites positioned at heavy traffic crossroads (S1, S4, and S5), while S3 shows moderate pollution. PM2.5 data show serious pollution at S4, moderate pollution at S1 and S5, and slight pollution at S3. The Fe data show slight pollution at all sampling sites.

Table 5. The calculated PI data for each parameter at each sampling site

Tabela 5. Izračunati PI podaci za svaki parametar na svakom mestu uzorkovanja

Site	PI _{TSP}	PI _{PM10}	PI _{iPM2.5}	PI _{FeTSP}	PI _{FePM10}	PI _{FePM2.5}	PI _{Femoss}
S1	4.59	5.53	2.14	1.07	1.11	1.16	1.33
S 3	2.27	2.38	1.68	1.05	1.08	1.23	1.15
S4	7.58	8.62	3.45	1.12	1.25	1.40	1.82
S5	6.65	8.26	2.50	1.08	1.16	1.16	1.49



3.1. Multivariate analysis

The Pearson correlation data between the pairs of parameters are shown in Table 6.

As is shown in Table 6, the parameters under investigation show very good and significant

correlations (r > 0.8, p < 0.05), indicating strong associations between parameters. Cluster analysis was performed for better visualization of the manner of associations between parameters (Fig. 4a) and monitoring sites (Fig. 4b).

1	Variables 2	Ν	Correlation	95% CI for ρ	P-Value
PM10	TSP	5	0.996	(0.942, 1.000)	0.000
PM2.5	TSP	5	0.958	(0.493, 0.997)	0.010
FeTSP	TSP	5	0.942	(0.353, 0.996)	0.017
Fe _{PM10}	TSP	5	0.963	(0.541, 0.998)	0.008
Fe _{moss}	TSP	5	0.963	(0.539, 0.998)	0.008
PM2.5	PM10	5	0.931	(0.273, 0.996)	0.021
Fe _{TSP}	PM10	5	0.918	(0.188, 0.995)	0.028
Fe _{PM10}	PM10	5	0.938	(0.323, 0.996)	0.018
Fe _{moss}	PM10	5	0.937	(0.314, 0.996)	0.019
Fe _{TSP}	PM2.5	5	0.985	(0.778, 0.999)	0.002
Fe _{PM10}	PM2.5	5	0.998	(0.973, 1.000)	0.000
Fe _{moss}	PM2.5	5	0.995	(0.921, 1.000)	0.000
Fe _{PM10}	Fe _{TSP}	5	0.986	(0.794, 0.999)	0.002
Fe _{PM2.5}	Fe _{TSP}	5	0.895	(0.063, 0.993)	0.040
Fe _{moss}	Fe _{TSP}	5	0.963	(0.533, 0.998)	0.009
Fe _{moss}	Fe _{PM10}	5	0.992	(0.884, 1.000)	0.001
Fe _{moss}	Fe _{PM2.5}	5	0.841	(-0.160, 0.989)	0.074

Table 6. The results of Pearson correlation dataTabela 6. Rezultati Pirsonove korelacije

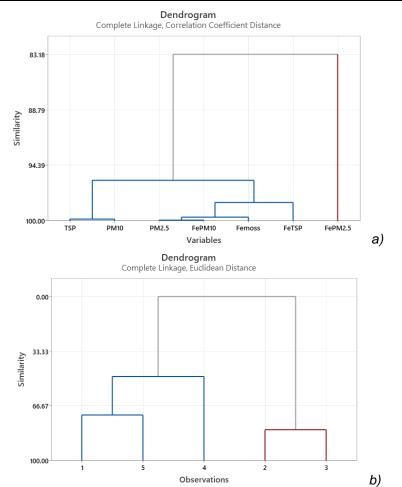


Figure 4. Dendrogram of cluster analysis performed for better visualization of the manner of associations between parameters (a) and monitoring sites (b)

Slika 4 Dendrogram klaster analize urađen radi bolje vizuelizacije načina povezanosti parametara (a) i mesta praćenja (b)

All parameters, except the Fe content in PM2.5 (Fepm2.5), are grouped (Fig. 4a) in Cluster 1 with a very high similarity level, higher than 90%, between them. Fepm2.5 shows a high similarity, higher than 81%, with the parameters of Cluster 1. It supports similar activities, mostly in the construction industry, traffic emissions, soil dust emissions, residential and commercial activities, and urban waste management that affect the discrimination between two clusters. Based on the matrix data of the investigated parameters, sampling sites are grouped into two different clusters with high differences between them. The less polluted residential sites S2 and S3 showed a high degree of similarity and are grouped in the same cluster with about 74% similarity, while traffic sites S1, S4, and S5 are grouped in the next cluster. The similarity level between the two clusters is very low, close to zero, indicating big differences in their pollution levels.

4. CONCLUSIONS

This research reveals the diurnal mean concentrations of particulate matter (PM2.5 and PM10) and the Fe concentrations in PMs and moss transplants evaluated at five sampling sites in Tirana city. The content of PMs exceeds the limit values suggested by WHO and EU Directives. Fe concentrations associated with TSP and PM10 on the roadside compared to the background site increased by about five to ten times, while those associated with PM2.5 were about four times higher. The increase in PMs' content at heavy traffic crossroads sites compared to background data suggests a high effect of traffic on the generation of PMs and an additional health risk for people living near the crossroads and heavy traffic sites. Major sources of PM10 could be geological material, soil dust and road dust emissions, traffic emissions, and the construction industry. From the location of monitoring sites and the emission inventory of PM2.5 in Tirana city, we suggest that the main sources of PM2.5 at crossroads could be dominated by mobile source emissions, and in residential areas by household activities, and other sources in the city could be from open burning and secondary species.

This is a preliminary study that shows a clear view of environmental problems caused in the city by different emissions that require an extension of the study in time and space. However, this research is noteworthy because its findings require some crucial improvements in monitoring systems and program design that can help evaluate the processes and factors that affect air quality and their short- or long-term effects on the health of those who live in polluted areas. A limitation exists in the findings of this study as the data analyzed here are derived from daily measurements during only three sequences of traffic peaks (morning, midday, and evening) in the city and are not extended in time under different weather conditions. It may be affected by uncontrolled time-varying data.

Acknowledgments

The author express the gratitude to Mira Aničić Urosevic, University of Belgrade for providing the moss transplants packed in bags. The authors thank Master students from department of Chemistry for their help in fieldwork and GFAAS analysis of samples.

5. REFERENCES

- B.Grobéty, R.Gieré, V.Dietze, P.Stille (2010) Airborne Particles in the Urban Environment. Edited in "Elements". 6(4), 229-234. https,//doi.org/ 10.2113/gselements.6.4.229
- [2] F.Kunt, Z.C.Ayturan, F.Yümün, I.Karagönen, M.Semerci, M.Akgün (2023) Modeling and Assessment of PM10 and Atmospheric Metal Pollution in Kayseri Province, Turkey. Atmosphere., 14(2), 356. https,//doi.org/10.3390/atmos14020356
- [3] C.Molina, A.R.Toro, S.R.G.Morales, C.Manzano, A.Manuel, M.A.Leiva-Guzmán (2017) Particulate matter in urban areas of south-central Chile exceeds air quality standards. Air Qual Atmos Health., 10, 653–667. https://doi.org/10.1007/s11869-017-0459-y
- [4] F.Cozzi, G.Adami, P.Barbieri, E.Reisenhofer, P.Apostoli, M.Bovenzi (2010) Toxic elements content in PM10 samples from a coastal area of the Northern Adriatic Sea. Cent. Eur. J. Chem, 8(5),1014–1026. doi: 10.2478/s11532-010-0074-3
- [5] Jin, L. Luo, X. Fu, P. Li, X. (2017) Airborne particulate matter pollution in urban China, a chemical mixture perspective from sources to impacts. National Science Review., 4, 593–610. doi: 10.1093/nsr/nww079
- [6] J.S.Pastuszka, W.Rogula-Kozłowska, E.Zajusz-Zubek (2010) Characterization of PM10 and PM2.5 and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. Environ Monit Assess., 168, 613–627. doi:10.1007/s10661-009-1138-8
- H.Harmens, D.Norris, G.Mills and the participants of the moss survey (2013) Heavy metals and nitrogen in mosses, spatial patterns in 2010/2011 and longterm temporal trends in Europe 2013. ICP Vegetation Programme Coordination Centre CEH Bangor UK. https,//icpvegetation.ceh.ac.uk/sites/default/ fles/Heavy%20metals%20and% 20nitrogen%20in%20 mosses%20-%20spatial%20pat terns%20in%202010-2011.pdf
- [8] H.Harmens, D.A.Norris, K.Sharps, G.Mills, R.Alber, Y.Aleksiayenak, O.Blum, S-M.Cucu-Man, M.Dam, L. De Temmerman, A.Ene, J.A.Fernández, J.Martinez-Abaigar, M.Frontasyeva, B.Godzik, Z.Jeran, P.Lazo, S.Leblond, S.Liiv, SH.Magnússon, B.Maňkovská, G.Pihl Karlsson, J.Piispanen, J.Poikolainen, J.M.Santamaria, M.Skudnik, Z.Špirić, T.Stafilov,

Limitations

E.Steinnes, C.Stihi, I.Suchara, L.Thöni, L.Todoran, L.Yurukova, H.G.Zechmeister (2015) Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010. Environ Pollut., 200, 93–104. doi: 10.1016/j.envpol.2015.01.036

- [9] M.Lodenius (2013) Use of plants for biomonitoring of airborne mercury in contaminated areas. Environ Res., 125,113-23. doi:10.1016/j.envres.2012.10.014
- [10] A.Barandovski, T.Stafilov, R.Šajn, M.Frontasyeva, K.Bačeva Andonovska (2020) Atmospheric Heavy Metal Deposition in North Macedonia from 2002 to 2010 Studied by Moss Biomonitoring Technique. Atmosphere, 11, 929. Doi:10.3390/atmos11090929
- [11] P.Lazo, A.Kika, F.Qarri, L.Bekteshi, Sh.Allajbeu, T.Stafilov (2022) Air Quality Assessment by Moss Biomonitoring and Trace Metals Atmospheric Deposition. Aerosol and Air Qual. Res., 22(5), 220008. https,//doi.org/10.4209/aaqr.220008
- [12] P.Lazo, T.Stafilov, F.Qarri, Sh.Allajbeu, L.Bekteshi, M.Frontasyeva, H.Harmens (2019) Spatial and temporal trend of airborne metal deposition in Albania studied by moss biomonitoring". Ecological Indicators.101,1007-1017. doi.10.1016/j.ecolind.2018.11.053.
- [13] P.Lazo, E.Steinnes, F.Qarri, Sh.Allajbeu, S.Kane, T.Stafilov, M.Frontasyeva, H.Harmens (2018) Origin and spatial distribution of metals in moss samples in Albania, A hotspot of heavy metal contamination in Europe.Chemosphere., 190, 337-349. doi.10.1016/ j.chemosphere.2017.09.132
- [14] W.Schröder, S.Nickel, S.Schönrock, M.Meyer, W.Wosniok, H.Harmens, M.V.Frontasyeva, R.Alber, J.Aleksiayena, L.Barandovski, A.Carballeira, H. Danielsson, L.de Temmermann, B.Godzik, Z.Jeran, G. P.Karlsson, P.Lazo, S.Leblond, A.J.Lindroos, S.Liiv, S.H.Magnússon, B.Mankovska, J.Martínez-Abaigar, J.Piispanen, J.Poikolainen, I.V.Popescu, F. Qarri, J.M.Santamaria, M.Skudnik, Z.Špirić, T. Stafilov, E.Steinnes, C.Stihi, L.Thöni, H.T.Uggerud, H.G.Zechmeister (2016) Spatially valid data of atmospheric deposition of heavy metals and nitrogen derived by moss surveys for pollution risk assessments of ecosystems. Environ Sci Pollut Res. 23(11),10457-10476. doi: 10.1007/s11356-016-6577-5
- [15] M.Aničić Urošević, T.Milićević (2020) Moss bag biomonitoring of airborne pollutants as an ecosustainable tool for air protection Managem.ent, Urban vs. agricultural scenario. Included in, Environmental Concerns and Sustainable Development Volume 1, Air, Water and Energy Resources. Editors, Vertika Shukla and Narendra Kumar Springer; p.29–60. (eBook) https,//doi.org/10.1007/978-981-13-5889-0
- [16] M.Aničić, M.Tomašević, M.Tasić, S.Rajšić, A. Popović, M.V.Frontasyeva, S.Lierhagen, E.Steinnes (2009a) Monitoring of trace element atmospheric deposition using dry and wet moss bags, Accumulation capacity versus exposure time. J Haz Mat,171(1-3),182–188.

DOI:10.1016/j.jhazmat.2009.05.112

[17] M.Aničić, M.Tasić, M.V.Frontasyeva, M.Tomašević, S.Rajšić, Z.Mijić, A.Popović (2009b) Active moss biomonitoring of trace elements with Sphagnum girgensohnii moss bags in relation to atmospheric bulk deposition in Belgrade Serbia. Environ Pollut, 157(2),673–679. DOI:10.1016/j.envpol.2008.08. 003

- [18] Á.Ares, J.R.Aboal, A.Carballeira, S.Giordano, P. Adamo, J.A.Fernández (2012) Moss bag biomonitoring, a methodological review. Sci Total Environ, 432,143–158. DOI: 10.1016/j.scitotenv. 2012.05.087
- [19] A.De Agostini, P.Cortis, A.Cogoni (2020) Monitoring of Air Pollution by Moss Bags around an Oil Refinery, A Critical Evaluation over 16 Years. Atmosphere, 11(3), 272–286. https,//doi.org/10. 3390/atmos11030272
- [20] P.Adamo, S.Giordano, S.Vingiani, R.Castaldo Cobianchi, P.Violante (2003) Trace element accumulation by moss and lichen exposed in bags in the city of Naples. (Italy) Environ Pollut, 122(1),91– 103. https//doi. org/10.1016/ s0269- 7491(02) 00277-4
- [21] G.Vuković, M.Aničić Urošević, Z.Goryainova, M.Pergal, S.Škrivanj, R.Samson, A.Popović (2015) Active moss biomonitoring for extensive screening of urban air pollution, Magnetic and chemical analyses. Sci Total Environ, 521–522, 200–210. https,//doi.org/10. 1016/j.scitotenv.2015.03.085
- [22] R.Hu, Y.Yan, X.Zhou, Y.Wang, Y.Fang (2018) Monitoring Heavy Metal Contents with Sphagnum junghuhnianum Moss Bags in Relation to Traffic Volume in Wuxi China. Int J Environ Res Public Health, 15(2),374–386. doi:10.3390/ijerph15020374.
- [23] L.Demková, L.Bobulská, J.Árvay, T.Jezný, L.Ducsay (2017) Biomonitoring of heavy metals contamination by mosses and lichens around Slovinky tailing pond. (Slovakia) J Environ Sci Health A Tox Hazard Subst Environ Eng. 52(1),30–36. doi:10.1080/10934529.2016.1221220
- [24] https,//www.iqair.com/world-air-quality-report
- [25] A.Kabata-Pendias, B.Szetke, (2019) Trace elements in abiotic and biotic environment. CRC Press, Taylor &Francis Group, p.468. https//doi.org/10.1201/ b18198
- [26] SIST EN-12341, 2014. (MAIN) Ambient Air Standard gravimetric method for the determination of the PM 10or PM2.5, mass concentration of suspended particulate matter. https://standards.iteh.ai/ catalog/standards/%20sist/ 5d138eac-4d44-4419-a069eb23d01a9b0c/sist-en-12341-2014
- [27] M.Aničić Urošević, P.Lazo, T.Staflov, M.Nečemer, K.Bačeva Andonovska, B.Balabanova, G. Hristozova, S.Papagiannis, C.Stihi, M.Suljkanović, Z.Špirić, V.Vassilatou, K.Vogel-Mikuš (2023) Active biomonitoring of potentially toxic elements in urban air by two distinct moss species and two analytical techniques, a pan-Southeastern European study. Air Qual Atm & Health, https//doi.org/ 10.1007/s11869-022-01291-z
- [28] M.C.Sorrentino, F.Capozzi, K.Wuyts, S.Joosen, V.K.Mubiana, S.Giordano, R.Samson, V.Spagnuolo, (2021) Mobile biomonitoring of atmospheric pollution, a new perspective for the moss-bag approach. Plants 10, 2384. https// doi.org/10.3390/ plants10112384
- [29] S.Esposito, S.Loppi, F.Monaci, L.Paoli, A.Vannini, S.Sorbo, V.Maresca, L.Fusaro, E.Asadi Karam, M.Lentini, A.De Lillo, Conte, P.Cianciullo, A.Basile (2018) In-field and in-vitro study of the moss Leptodictyum riparium as bioindicator of toxic metal pollution in the aquatic environment, ultrastructural damage, oxidative stress and HSP70 induction.

PLoS ONE. 13(4),e0195717. https//doi.org/ 10.1371/ journal.pone.0195717

- [30] F.Capozzi, S.Giordano, J.Aboal, P.Adamo (2016) Best options for the exposure of traditional and innovative moss bags, A systematic evaluation in three European countries. Env Poll, 214,362–373. https//doi.org/10.1016/ j.envpol.2016.04.043
- [31] G. Vuković, M.Aničić Urošević, S.Škrivanj, T. Milićević, D.Dimitrijević, M.Tomašević, A.Popović, (2016) Moss bag biomonitoring of airborne toxic element decrease on a small scale, A street study in Belgrade Serbia. Sci Total Environ, 542,394–403. https//doi.org/10.1016/j.scitotenv.2015.10.091
- [32] M.Rivera, H.Zechmeister, M.Medina-Ramón, X. Basagaña, M.Foraster, L.Bouso, T.Moreno, P. Solanas, R.Ramos, G.Köllensperger, A.Deltell, D. Vizcaya, N.Künzli (2011) Monitoring of heavy metal concentrations in home outdoor air using moss bags. Environ Pollut, 159(4),954–962. https://doi.org/ 10. 1016/j.envpol.2010.12.004
- [33] P.J.Temple, D.L.McLaughlin, S.N.Linzon, R.Wills (1981) Moss bags as monitors of atmospheric deposition. J.Air Pollut Control Assoc, 31(6),668– 670.https//doi.org/10.1080/00022470.1981.1046526
- [34] Y.Chen, H.X.Zhao, Z.H.Xie, H.Y.Huang, S.Y.Zang, B.Lian (2015) Heavy metal pollution characteristics in the Kaili coal mining region, Guizhou province, China. J Resid Sci Technol, 12, S123-S131. doi:10.12783/ issn.1544-8053/12/S1/18
- [35] A.Michalik (2008) The Use of Chemical and Cluster Analysis for Studying Spring Water Quality in Świętokrzyski National Park. Polish J. of Environ., 17(3),357-362.
- [36] H.Charreire, C.Weber, B.Chaix, P.Salze, R.Casey, A.Banos, D.Badariotti, E.Kesse-Guyot, S.Hercberg, C.Simon, J.M Oppert (2012) Identifying built environmental patterns using cluster analysis and GIS, Relationships with walking, cycling and body

mass index in French adults. Int J Behav Nutr Phys. Act, **9**,59. https://doi.org/10.1186/1479-5868-9-59

- [37] M.Cetin (2015) Using GIS analysis to assess urban green space in terms of accessibility, case study in Kutahya. International Journal of Sustainable Development & World Ecology, 22(5),420-424. https,//doi.org/ 10.1080/13504509.2015.1061066
- [38] M.F.Goodchild (2009) Geographic information systems and science, Today and tomorrow. Annals of GIS., 15(1), 3-9. https://doi.org/10.1016/ j.proeps. 2009.09.160
- [39] Directive, 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe. Website, europa.eu
- [40] C.W.Tessum, M.W.Anenberg, S.C.Chafe, Z.A. Henze, D.K.Kleiman, G.Kheirbek, I.Marshall, J.D. Tessum (2022) Sources of ambient PM2.5 exposure in 96 global cities. Atmospheric Environment. 286, 119234. https://doi.org/10.1016/j.atmosenv. 2022. 119234
- [41] X.Zhang, K.Zhang, H.Liu, W.Lv, M.Aikawa, B.Liu, J. Wang (2020) Pollution sources of atmospheric fine particles and secondary aerosol characteristics in Beijing. J.Environ Sci., 95, 91-98. https//doi.org/ 10.1016/j.jes.2020.04.002
- [42] G.D.Thurston, K.Ito, R.Lall (2011) A Source Apportionment of U.S. Fine Particulate Matter Air Pollution. Atmos Environ (1994), 45(24),3924-3936. doi: 10.1016/j.atmosenv.2011.04.070.
- [43] G.D. Thurston, J.D. Spengler (1985) A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmos Environ., 1,9–25. https//doi.org/10.1016/0004-6981(85)90132-5
- [44] M.Abu-Allaban, D.H.Lowenthal, A.W.Gertler, M. Labib (2007) Sources of PM10 and PM2.5 in Cairo's ambient air. Environ Monit Assess, 133, 417–425. DOI:10.1007/s10661-006-9596-8

IZVOD

PRELIMINARNA STUDIJA O PROCENI KVALITETA VAZDUHA U TIRANI, ALBANIJA

Koncentracije čestica i Fe u česticama u vazduhu i presađenoj mahovini su istražene da bi se procenio kvalitet vazduha grada Tirane. Izveden je u leto 2021. i u zimu 2020–2021. Čestice različitih veličina (PM2,5 i PM10) su sakupljene na filterima od staklenih vlakana obloženih teflonom. Fe je određen u PM i transplantacijama mahovine, poslednji su bili izloženi dva meseca na istom mestu praćenja kao i PM. Merenja su vršena u područjima sa gustim saobraćajem tokom leta pod relativno visokim temperaturama vazduha, do 23°C, što može uticati na visoke koncentracije čvrstih čestica u vazduhu, a samim tim i na visok nivo Fe. Statistička analiza je korišćena za razmatranje rezultata čestica i gvožđa u čvrstim česticama i mahovini. Veća koncentracija Fe je nađena u ukupnim suspendovanim česticama (TSP), a niža koncentracija u manjim česticama. Podaci o koncentracijama su upoređeni sa vrednostima preporučenim u evropskim direktivama. Koncentracije svih ispitivanih parametara bile su veće od dozvoljenih za ruralna i stambena područja i niže od preporučenih vrednosti za industrijska područja. Korelaciona analiza je pokazala visoke i značajne korelacije (R > 0,8, p < 0,05) između koncentracija Fe u transplantaciji mahovine i čestice, pokazujući visok efekat čestica na Fe u vazduhu. Može povećati izloženost ljudi udisanjem i dovesti do štetnih zdravstvenih problema. Za to su potrebne jače mere za poboljšanje kvaliteta vazduha u gradu.

Ključne reči: kvalitet vazduha, PM, kese od mahovine, raskrsnice puteva, stambeno naselje, Tirana

Naučni rad Rad prijavljen: 30.04.2023. Rad prihvaćen: 19.07.2023. Rad je dostupan na sajtu: www.idk.org.rs/casopis © 2023 Authors. Published by Engineering Society for Corrosion. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/)