AIR POLLUTION ANALYSIS AND CONTINUOUS MONITORING OF PARTICULATE MATTER ($PM_{2.5}$) IN AN URBAN AREA

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Abstract

Tirana is a highly populated city with a significant number of vehicles, making the control and management of air pollutants crucial. Primary pollutants originate from various sources, including industrial factories and different combustion sources. Correlation analysis, along with the determination coefficient R^2, reveals strong relationships among certain primary pollutants, particularly organic ones. Through this analysis we determined if the pollutants share a common source. High values indicate a strong connection between pollutants, suggesting a shared source. We analyzed daily median concentrations for $PM_{2.5}$ (average yearly concentration 8 µg/m³) and PM_{10} (18 µg/m³) dataset for two urban sites in Tirana, available from the World Air Quality Index (WAQI). We evaluated that during years 2020 - 2024 the average daily concentration of $PM_{2.5}$ varied each year, with higher peaks in winter due to biomass burning reaching the highest median daily value 50 µg/m³ in January 2021. Concentration of PM_{10} was every year double the concentration of $PM_{2.5}$. We also conducted continuous 24 hours measurements in an urban area in Tirana using a low volume sampler device. To ensure accurate measurements, the equipment was placed 17 meters above the ground in an open space collecting information regarding not only $PM_{2.5}$ but also temperature and pressure, twice weekly in Mars until 15 April. Consistently measured a flow rate of 2.3 m^3/h and an average $PM_{2.5}$

concentration of 20 μg/m³ across several days. While temperature max and min values were 23.9 °C and 10.8 °C. The Air Quality Index calculated for $PM_{2.5}$ 24-hour measurements was 68 indicating moderate levels.

***Key word**: Primary pollutants, Low Volume Sampler device, correlation analysis (R), determination coefficient (R^2).*

Përmbledhje

Tirana është një qytet shumë i populluar me një numër të konsiderueshëm automjetesh, gjë që e bën shume të rëndësishme kontrollin dhe menaxhimin e ndotësve të ajrit. Ndotësit parimar rrjedhin nga burime të ndryshme, duke përfshirë fabrikat industriale dhe djegien e karburantit. Analiza e korrelacionit, së bashku me koeficientin e përcaktimit R^2, tregoi marrëdhënie të forta midis disa ndotësve parimar, veçanërisht atyre organikë. Nëpërmjet kësaj analize ne përcaktuam nëse ndotësit ndajnë një burim të përbashkët. Vlerat e larta treguan një lidhje të fortë midis ndotësve, duke sugjeruar një burim të përbashkët. Ne analizuam përqendrimet mesatare ditore për grupin e të dhënave $PM_{2.5}$ (përqendrimi mesatar vjetor 8 μg/m³) dhe PM_{10} (18 μg/m³) për dy zona urbane në Tiranë, të disponueshme nga Indeksi Botëror i Cilësisë së Ajrit (WAQI). Ne vlerësuam se gjatë viteve 2020-2024 përqendrimi mesatar ditor i $PM_{2.5}$ ndryshonte çdo vit, me vlera më të larta në dimër për shkak të djegies së biomasës duke arritur vlerën mesatare ditore më të lartë 50 μg/m³ në Janar 2021. Përqendrimi i PM_{10} ishte çdo vit ishte dyfishi i përqendrimit të $PM_{2.5}$. Gjithashtu kemi kryer matje të vazhdueshme në një zonë urbane në Tiranë duke përdorur një pajisje kampionimi me volum të ulët. Për të siguruar matje të sakta, pajisja u vendos 17 metra mbi tokë në një hapësirë të hapur duke mbledhur informacion jo vetëm në lidhje me $PM_{2.5}$, por edhe për temperaturën dhe presionin, dy herë në javë në Mars dhe Prill. Matur në mënyrë të vazhdueshme me një shpejtësi të rrjedhjes prej 2.3 m^3/h, vërejtëm një përqendrim mesatar $PM_{2.5}$ prej 20 μg/m³. Ndërsa vlerat maksimale dhe minimale të temperaturës ishin 23,9 °C dhe 10,8 °C. Indeksi i cilësisë së ajrit i llogaritur për matjet 24 orëshe $PM_{2.5}$ ishte 68 që tregon nivele jo të shëndetshme.

***Fjalë kyçe:** Ndotësit primar, aparati mates ajri, analiza e korrelacionit (R), koefiçenti i përcaktimit (R^2).*

Introduction

Atmosphere is composed of a mixture of gases (N_2, O_2, Ar, CO_2, Ne, He, CH_4, Kr, H_2, N_2O, O_3, water vapor. *(John M. Wallace, Peter V. Hobbs 2006)* While transportation is very important aspect of modern life, enabling us to work, learn, and connect, its reliance on fossil fuels comes at a cost to public health. Air pollution from vehicles not only harms human lungs, but also damages vegetation and disrupts ecosystems. This concerning issue has gained significant attention in recent years (Deb & Tsay, 2018). The presence of airborne contaminants, like pollutants from emissions, can negatively impact human health, well-being, and the environment especially in highly populated urban areas (*Premti et al 2014).*

Clean Air Act of 1970 established the National Ambient Air Quality Standards to address six so-called “criteria air pollutants” (SO_2, PM, CO, O_3, NO_2, Pb, CO_2). PM is a common physical classification of particles found in air, such as dust, dirt, soot, smoke, and liquid droplets. Unlike other US criteria pollutants [O_3, CO, SO_2, NO_2 and lead (Pb)], PM is not a specific chemical entity but is a mixture of particles from different sources and of different sizes, compositions, and properties. Primary pollutants are air pollutants emitted directly from a source. *(Daniel A. Vallero.2008).*

Hydrocarbons are highly emitted components in urban air because of combustion, solvent and fuel evaporation and tank leakage. Among them, most of the aromatic compounds are listed as toxic air contaminants (e.g. benzene) or potential toxic air contaminants (e.g. toluene, xylenes). During daytime hours, once released into the atmosphere, aromatic components undergo OH oxidation, and thus participate in the formation of urban and suburban photochemical smog. The total ozone attributable to each organic compound is influenced greatly by the relative concentration of each species *(Anne Monod.et.al 2000).* For this reason our study was focused on experimental determination of primary air pollutant correlations between these pollutants and determination of R^2 (coefficient of determination).

Many studies use correlation analysis to explore the degree association between variables, a correlation analysis become useful to explore the associative relationship between independent and dependent variables. *(Senthilnathan, Samithamby 2019).* The coefficient of determination, R^2, is well-defined in linear regression models, and measures the proportion of variation in the dependent variable explained by the predictors included in the model. *(Zhang, Dabao 2016)*. Xylene and ethylbenzene are very well correlated for heavy loaded urban, traffic, and liquid fuel samples. As with m- and p-xylene, o- and m-xylene are also well correlated. Toluene and benzene are well correlated throughout traffic, biomass burning and fuel samples. *(Anne Monod.et.al 2000).*

Destruction of stratospheric ozone caused by relatively small atmospheric concentrations of chlorofluorocarbons has vividly illustrated the capacity of human activity to alter our atmosphere in a manner that has significant and far-ranging effects. There is similar concern for the effects of greenhouse gases on the earth's climate. (*Finlayson-Pitts, B. J., & Pitts Jr., J. N., 2000)*

Methodology

Statistical assessment and their correlation

Correlation analysis, along with the determination coefficient R^2, reveals strong relationships among certain primary pollutants. Using the data obtained from ISHP on primary air pollutants in two urban areas of Tirana in 2017-2018, we conducted a comprehensive analysis to gain insights into the intricate relationship between these pollutants. By examining the concentrations and patterns of these pollutants, we aimed to uncover potential correlations.

WAQI data analysis

Particulate matter (PM) holds significant importance in relation to primary pollutants due to its role as a carrier with direct impact on human health. PM, particularly $PM_{2.5}$ and PM_{10}, act as carriers for primary pollutants like SO_2, NO_2, benzene, etc., facilitating their dispersion and infiltration into the atmosphere. This interaction amplifies the adverse effects of primary pollutants by extending their reach and exposure duration. Based on the WAQI data 2020-2024, we have conducted an analysis of the daily average concentrations for the $PM_{2.5}$ (with an annual average concentration of 8 $\mu g/m^3$) and PM_{10} (with a concentration of 18 $\mu g /m^3$) data sets in two urban center areas in Tirana.

Experimental Application

Air filters were collected in an urban area in Tirana (Faculty of Natural Sciences, UT) using a Low Volume Sampler device ensuring accurate air pollutant measurements, the equipment was placed 17 meters above the ground in an open space collecting information regarding not only $PM_{2.5}$ but also temperature and pressure, twice weekly until 15 April. Equipment used for the performance of measurements is LVS sampler (fig.1) that can operate at temperatures of approximately –30 °C up to more than 50°C under all weather conditions. The flowrates are controlled in terms of operating –m^3/h ($2.3 m^3/h$). The flow rates as well as the sampled volumes are displayed and recorded in terms of operating-m^3/h resp. operating-m^3 (related to ambient conditions, each) and additionally recorded in terms of standard-m^3/h resp. standard-m^3 (related to 0 °C and 1013 mbar, each).

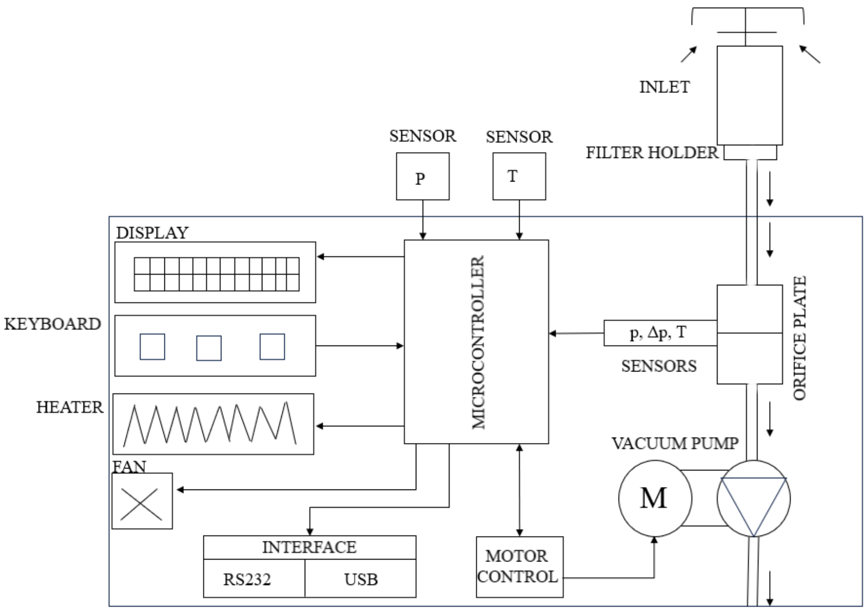

Figure 1: Block diagram LVS

Filters used for 24 hour measurements were weighed before and after collection. Further, all relevant data (including continuous measurements of temperature and pressure) is displayed and recorded on the USB stick with data logger function. In case of a power failure, all data stored in the microcontroller and in the system's, memory will be safe for several years thanks to a built-in high-capacity battery. The filter cassettes are placed in the sampling inlet directly downstream the impactor.

Results and discussion

The data obtained from ISHP (Public Health Institute of Tirana), indicate distinct seasonal variations in the emission levels of various air pollutants. Tirana exhibits seasonal variations in air pollutant concentrations. SO_2 and O_3 peak in June (23,35 μg/m^3 and 41,5 μg/m^3, respectively), while CO emissions are lowest (0.56 μg/m^3) compared to their February peak (1,144 μg/m^3). SO_2 reaches a minimum in August (2,12 μg/m^3).

Interestingly, NO_2 shows an opposite trend to O_3. December sees the highest NO_2 emission (47,9 μg/m^3) and the lowest O_3 emission (1,5 μg/m^3). October records the lowest NO_2 emission (47,9 μg/m^3). Volatile Organic Compounds (VOCs) display a different seasonal pattern. Toluene, p-xylene, o-xylene, and ethylbenzene (T, p-x, o-x, and EB) peak together in October (12,74 μg/m^3 T, 14,77 μg/m^3 p-x, 3,51 μg/m^3 o-x, 2,94 μg/m^3 EB) and reach their lowest concentrations in December (5,45 μg/m^3 T, 7,35 μg/m^3 p-x, 1,47 μg/m^3 o-x, 1,43 μg/m^3 EB). In contrast, benzene follows a distinct pattern, peaking in November (4,26 μg/m^3) and having its minimum in May (2,84 μg/m^3).

This suggests different emission sources or atmospheric behavior for benzene compared to the other VOCs. The seasonal variations of T, p-x, o-x, and EB indicate a stronger relationship among them than with benzene.

When different pollutants show maximum or minimum emission values in the same month, they have a connection between them based on source emitted. To estimate and determine the common source we used the correlation analysis and the coefficient of determination.

Table 1. Correlation analysis for the parameters monitored by the automatic station installed in an urban area I, year 2017-2018.

	SO_2	O_3	CO	NO_2	Benzene	Toluen	p-xylene	o-xylene	Ethylb
SO_2	1								
O_3	-0,17	1							
CO	0,15	-0,7	1						

NO_2	0,22	-0,8	0,36	1					
Benzene	-0,4	-0,3	0,33	0,03	1				
Toluen	-0,4	0,4	-0,26	-0,7	0,5	1			
p-xylene	-0,3	-0,25	0,22	-0,19	0,74	0,75	1		
o-xylene	-0,35	0,01	0,16	-0,42	0,74	0,86	0,9	1	
Ethylb	-0,4	-0,04	0,15	-0,37	0,76	0,83	0,9	0,98	1

Strong organic pollutants are those that are well correlated with each other with R ranging from 0.741 to 0.986 and R^2 0.25 to 0.974. Based on the fact, where these pollutants have their maximum and minimum emission values in the same months, the correlation analysis confirms that these pollutants share quantitatively the same source. (*Anne Monod.et.al 2000).*

Likewise, there is a slight correlation between SO_2 and CO, NO_2 (R values 0.155 and 0.221). Although correlation is very small, it indicates that a small portion of these pollutants may come from the same source. Additionally, other pollutants also show some degree of correlation. For example, there is a correlation between O_3 and toluene as well as CO with NO_2, benzene, p-xylene, o-xylene, and Ethylbenzene. NO_2 is related with benzene.

Table 2. R^2 (coefficient of determination) for the parameters monitored by the automatic station installed in an urban area I, year 2017-2018.

	SO_2	O_3	CO	NO_2	Benzene	Toluen	p-xylen	o-xylen	Eth-ylb
SO_2	1								
O_3	0,03	1							
CO	0,02	0,5	1						
NO_2	0,05	0,6	0,13	1					

Benzene	0,15	0,1	0,11	0,001	1				
Toluen	0,16	0,18	0,07	0,48	0,25	1			
p-xylen	0,10	0,06	0,05	0,04	0,55	0,82	1		
o-xylen	0,12	$1*10^{-3}$	0,02	0,18	0,55	0,74	0,82	1	
Ethylb	0,16	0,002	0,02	0,137	0,56	0,69	0,82	0,97	1

Parameters monitored by the automatic station installed behind ISHP (II). In this urban area of Tirana, it is a noticeable disparity in the measured pollutant values compared to those outlined in area I above, which pertains to a different location. It is noteworthy that an identical phenomenon is observed for VOC. These pollutants exhibit their highest emission peaks in August (9,3 µg/m^3 B, 11,9 µg/m^{3}T, 25,4 µg/m^{3}p-x, 14,4195 µg/m^3 o-x, 13,78 µg/m^3 EB), while reaching their lowest emission levels in February (0,23 µg/m^3 B, 0,25 µg/m^3 T, 0,1 µg/m^3 p-x, 0,02 µg/m^{3}o-x, 0,026 µg/m^3 EB).

However, it is important to note that benzene, unlike other VOCs in the area, doesn't conform to the same monthly pattern. The difference in pollutant emissions between different areas of Tirana can be attributed to a many factors. One significant factor is population density, as densely populated areas tend to have higher emissions due to increased human activity and energy consumption. Additionally, vehicular activity plays a crucial role, as areas with heavy traffic experience elevated emissions from vehicles.

Table 3. Correlation analysis for the parameters monitored by the automatic station installed behind ISHP, year 2017 (monthly averages).

	SO_2	**O_3**	**CO**	**NO_2**	**Benzene**	**Toluen**	**p-xylene**	**o-xylene**	**Ethylb**
SO_2	1								
O_3	0,16	1							
CO	0,74	0,55	1						

NO_2	0,32	-0,08	0,45	1					
Benzene	0,09	-0,26	-0,016	0,12	1				
Toluen	0,022	-0,27	-0,063	0,13	0,99	1			
p-xylene	-0,07	-0,32	-0,14	0,09	0,97	0,98	1		
o-xylene	-0,13	-0,29	-0,18	0,02	0,97	0,98	0,98	1	
Ethylb	-0,13	-0,30	-0,19	0,012	0,97	0,97	0,99	0,99	1

Table 4. R^2 (coefficient of determination) for parameters monitored and reported by ISHP in an urban area (II) year 2017-2018(monthly averages).

	SO_2	**O_3**	**CO**	**NO_2**	**Benzene**	**Toluen**	**p-xylen**	**o-xylen**	**Ethylb**
SO_2	1								
O_3	0,026	1							
CO	0,548	0,31	1						
NO_2	0,104	0,006	0,2	1					
Benzene	0,009	0,06	0,0003	0,014	1				
Toluen	0,0005	0,07	0,0004	0,017	0,98	1			
p-xylen	0,006	0,1	0,019	0,0085	0,95	0,96	1		
o-xylen	0,016	0,08	0,035	0,0004	0,94	0,97	0,97	1	
Ethylb	0,017	0,09	0,035	0,0001	0,94	0,95	0,98	0,99	1

Our statistical analysis revealed distinct seasonal patterns in air pollutant emissions. December peak emissions for SO_2 (25,6 µg/m^3) and CO (1,08 µg/m^3). Conversely, February saw minimal SO_2 emissions (1,76 µg/m^3) coinciding with the highest O_3 level (16,5 µg/m^3). Similarly, May had the lowest CO emissions (0.31 µg/m^3) while September had the lowest O_3

emissions (3,2 µg/m^3). NO_2 emissions peaked in October (91,67 µg/m^3) and were lowest in June (9,4 µg/m^3). The correlation analysis (Table 3) provided insights into potential emission sources.

The weak correlation between SO_2 with O_3 and NO_2 suggests a limited association, while the stronger correlation between SO_2 and NO_2 implies a more significant link. Interestingly, SO_2 showed weak correlations with benzene and toluene. However, a strong correlation with CO points towards a possible common source. O_3 exhibited a moderate correlation with CO but lacked any significant correlation with organic pollutants. CO displayed a moderate correlation with NO_2 but no significant correlation with VOCs.

On the other hand, NO_2 had weak correlations with p-xylene, o-xylene, and ethylbenzene but a stronger correlation with benzene and toluene. The high degree of correlation observed within the VOC group is supported by the R^2 values, suggests a shared source for these organic pollutants.

Based on the WAQI data 2020-2024 the figures below show the concentrations of $PM_{2.5}$ and PM_{10} at 2 other urban stations in Tirana during 2021. Both figure 2 and 3 show that during winter we experience the highest concentrations of particulate matter due to the main source of biomass burning. During 2021 we observed several peaks that coincide with dust trajectories identified coming from Africa.

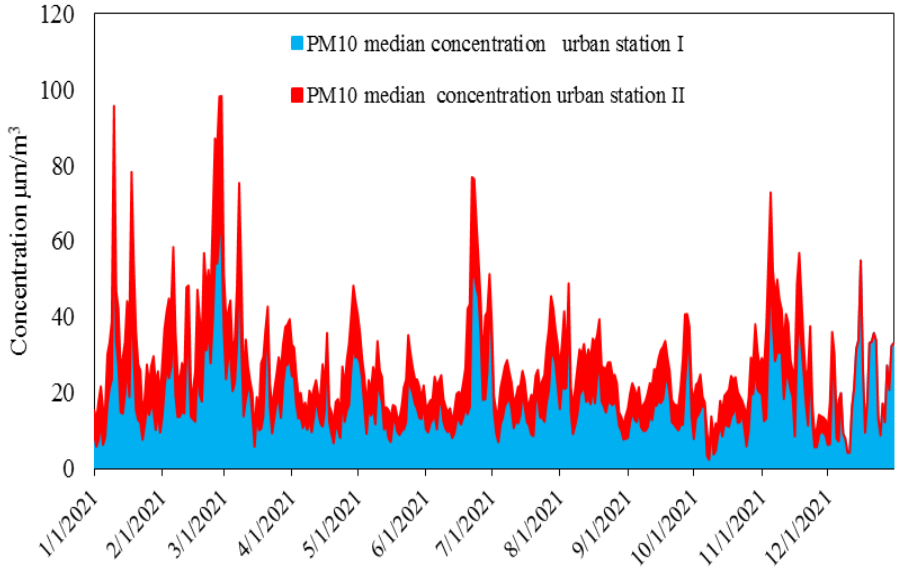

Figure 2. Concentration of PM_{10} in the area Jean d'Arc Boulevard (I), and 'Sensor Municipal Unit No. 7' (II).

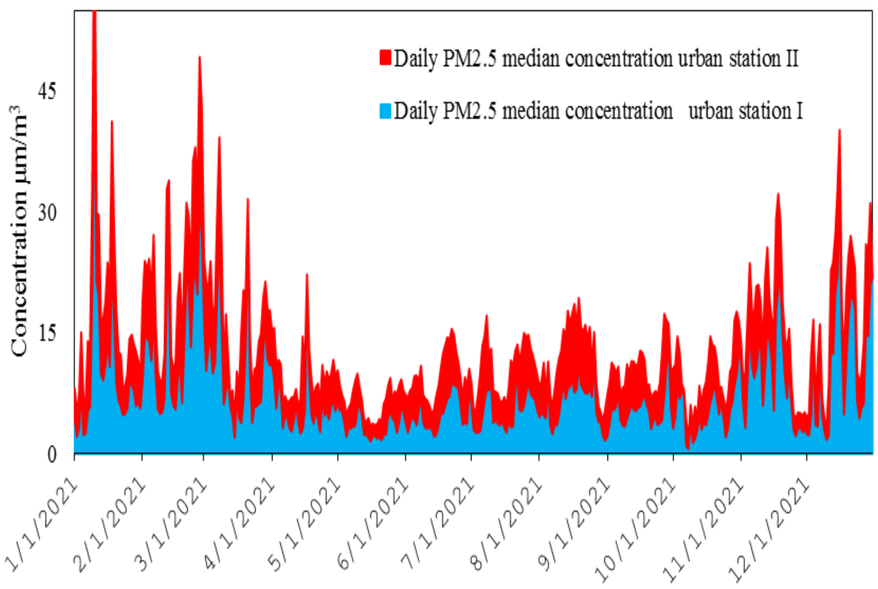

Figure 3. Concentration of $PM_{2.5}$ in the area Jean d'Arc Boulevard (I), and 'Sensor Municipal Unit No. 7' (II).

The Low Volume Sampler collected consistent data over several days from March until 15 April, averaging a daily $PM_{2.5}$ concentration of 20 µg/m³ at a flow rate of 2.3 m^3/h. It also recorded temperature fluctuations between a maximum of 23.9°C and a minimum of 10.8°C. When compared to the US EPA's Air Quality Index (AQI) for $PM_{2.5}$ https://www.epa.gov/air-quality, a 20 µg/m³ concentration translates to an AQI of 68. This falls under the category of "*Unhealthy for Sensitive Groups*".

This means people with existing respiratory or cardiovascular conditions, as well as the elderly, experience aggravated symptoms like coughing or wheezing. Long-term exposure at these levels increase the risk of premature mortality in these high-risk groups. While our study in Tirana exceeded the WHO guideline of 10 µg/m³, air quality in other parts of the Western Balkans faces similar challenges (World Bank, 2020). Bosnia and Herzegovina struggles with $PM_{2.5}$ levels exceeding national and WHO limits. The estimated population-weighted average annual $PM_{2.5}$ concentration in FBiH (30 µg/m³) is significantly higher than what we observed in Tirana.

Air quality data for Italy and Greece show mixed results. While some areas show moderate $PM_{2.5}$ levels comparable to Tirana, others experience higher concentrations. For instance, studies in northern Italy have documented levels exceeding 30 µg/m^3 (Amato et al. 2016) while in Greece has been reported average daily values 14.2 µg/m^3 (Grivas et al. 2018). PM_{10} concentrations in North Macedonia consistently surpassed limit values. $PM_{2.5}$ data, though limited, indicates substantial exceedances of the annual limit value (25 µg/m³). The estimated population-weighted average annual $PM_{2.5}$ concentration varies greatly depending on location, with highly polluted areas reaching 37 µg/m³. $PM_{2.5}$ and PM_{10} concentrations in Kosovo exceeded limits at several monitoring stations.

The estimated population-weighted average annual $PM_{2.5}$ concentration falls within the range observed in our Tirana study (26–31 µg/m³). While our study in Tirana indicates concerning $PM_{2.5}$ levels, the situation appears to be a regional issue. Further research and collaborative efforts across the Western Balkans, alongside Italy and Greece, are likely necessary to address this shared challenge.

Conclusions

The continuous monitoring using a Low Volume Sampler in an urban area of Tirana from March to April 15th revealed an average daily $PM_{2.5}$ concentration of 20 µg/m³. This translates to an Air Quality Index (AQI) of 68, categorized as "Unhealthy for Sensitive Groups" according to the US EPA's standards.

Data from the World Air Quality Index (WAQI) for 2020-2024 suggests seasonal variations, with potentially higher peaks in winter due to factors like biomass burning. The WAQI data also indicates that PM_{10} concentrations consistently exceeded $PM_{2.5}$ concentrations, often doubling the $PM_{2.5}$ levels. While Tirana's $PM_{2.5}$ levels are concerning, the situation appears to be a wider issue across the Western Balkans.

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