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Metal Element Traces Sampled from Peri-Urban Road Verge Particulate Matter

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Abstract: The objective of this research is to analyze metal elements, such as Na (sodium), Mg (magnesium), Al (aluminum), Si (silicon), Pb (lead), K (potassium), Ca (calcium), and Fe (iron), found in dust particles within two distinct areas from which the samplings were taken. The first sampling was taken from the road verge of a highly trafficked road section, while the second sampling was taken from a residential garden area 90 m away from the road. Several metal elements were detected with a high difference in Si, which presented higher concentrations in the dust samples from the road verge area. Pb has only been detected in the samples taken from the road verge, which could be explained by residual remnants from old lead gasoline and wheel weights. Additionally, during the same investigation, airborne particulate matter (PM) concentrations were measured in comparison between the road verge and the garden area; this presented a substantial difference in the concentration levels, suggesting that dense vegetation is protecting and blocking a majority of airborne PM. A literature highlight of the health effects of different metal elements and PM concentrations is presented.

Keywords: metals in PM; dynamic light scattering measurement; microscopic analysis; PM concentrations; inhalable-, thoracic-, and alveolar-sized particles

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1. Introduction

1.1. Particulate Matter Generation and Its Effects upon Human Health

Urban PM is significantly influenced by road traffic, which is identified as a substantial contributor. The particulates emitted by vehicles primarily originate from exhaust emissions, although they can also stem from non-exhaust sources unrelated to the exhaust process [1,2]. Moreover, the Volkswagen emissions scandal that recently came to light underscores the necessity of implementing rigorous engineering measures to attain enhanced air quality [2,3]. The installation of catalytic converters on gasoline-powered vehicles has resulted in significant decreases in urban concentrations of carbon monoxide and benzene globally. However, even though their proven detrimental impact on human health is well documented, effective control measures are still required for particulate matter and nitrogen dioxide [4,5].

The initial particles, denoted as exhaust particles, originate from the combustion of fuel. Conversely, the final particles—categorized as non-emission particles—result from various sources, including the wear of brake pads and disks, the abrasion of tires against the road surface, and the resuspension of dust particles from the road [6].

Dust particles comprise natural substances that accumulate on road surfaces and can be lifted again due to wind and traffic movement. Despite the implementation of certain regulations and significant technological advancements in the automotive sector, which have successfully mitigated emissions from vehicle exhaust gases, these measures do not influence the emissions of particulate matter (PM).

While there is a prevailing agreement highlighting the role of vehicle exhaust emissions in generating fine particles [2,3], it is important to note that non-exhaust emissions contribute to both fine and coarse particles within the PM10 category, with coarse particles showing a significant presence in this context [3,4].

Hence, there has been a significant rise in the quantity of particulate matter (PM) emissions stemming from non-exhaust sources in recent years, which has given rise to a progressively alarming health concern [3,4].

Continued contact with different-sized particulate matter (PM2.5 and PM10) has shown a consistent association with increased mortality rates stemming from non-accidental causes. Comprehensive studies have uncovered elevated mortality risks associated with long-term exposure to indicators of both vehicle exhaust emissions (like PM2.5 absorbance) and emissions from sources other than vehicles (particularly zinc and copper). Furthermore, components such as nickel, vanadium, and silicon, which are part of PM10, have also been linked to heightened mortality risks [7]. Despite their relatively small quantities in comparison to other components, the available evidence indicates that metals exhibit greater toxicity than other chemical compounds [8,9].

The accumulation of wear particles depends on their size. These tiny fragments can either settle near the road, be partially drawn toward passing vehicles, or become airborne again due to wind. Estimates indicate that approximately 40–50% of these particles come from brake wear, while an additional 0.1–10% stem from vehicle tire wear. [10]. Particle size distribution of residues from light vehicle brake wear is reported with increased attention to avoid sampling biases [11].

In cases of intermittent motion, such as repeated braking, smaller wear particles tend to be generated [12,13]. Upon engaging the brakes, the interaction between the pads and the rotating components invariably leads to the liberation of wear particles. The nature of these released wear fragments can be influenced by various factors. While some of the dislodged wear debris might exhibit an affinity toward the vehicle itself under specific circumstances, a substantial portion is released into the atmosphere as airborne particles [14,15].

Nanoparticles present in the atmosphere—particularly those with diameters below 300 nm—hold significant implications for both air quality control efforts and the scientific community, as they are associated with detrimental impacts on public health. Notably, a specific category of nanoparticles found in the emissions of diesel fuel engines—which a considerable portion of the population encounters on a daily basis—has been newly designated as a human carcinogen, which increases people's risk of developing lung cancer [16].

Based on the accumulated knowledge, an accurate assessment of the total particulate matter (PM) emissions arising from both internal combustion engine vehicles (ICEVs) and electric vehicles (EVs) has yet to be achieved through empirical analysis. Therefore, in this research [17], a comprehensive evaluation was undertaken involving a gasoline-powered ICEV, a diesel-powered ICEV, and an EV, all sharing identical body structures.

Emission factors (EFs) for exhaust PM were derived from three different vehicles and were classified into primary and secondary PM. Secondary PM refers to particles generated in the atmosphere through a sequence of physical and chemical reactions involving gases such as nitrogen oxides (NOx), sulfur dioxide (SO2), and ammonia (NH3), often catalyzed by sunlight [18,19]. EFs were computed both directly as PM and through key secondary PM gravimetric methods. These methods utilized conversion factors to translate precursor gases like NOx, SO2, and NH3 into PM.

On the non-exhaust emissions front, the resulting EFs were established and quantified through experimental methods and categorized based on their origins, such as brake wear, tire wear, road wear, or the resuspension of road dust. By amalgamating these diverse experimental findings, a comparison of PM emissions among the three vehicle types was made possible.

1.2. Presence of Metals in Particulate Matter and Their Negative Impact on Human Health

Urban road dust and surface soils can serve as carriers of heavy metals that possess the capacity to infiltrate the human body through diverse pathways like ingestion, direct inhalation, and skin contact. Such exposure to heavy metals has been linked to a variety of adverse health consequences. Notably, the issue of lead contamination stands out, with a recent global assessment attributing over 674,000 deaths to lead exposure in 2010 alone.

Excessive interaction with heavy metals can precipitate a range of detrimental health effects, encompassing impacts on the nervous, skeletal, circulatory, enzymatic, endocrine, and immune systems. A case in point is the inhalation of soil dust enriched with cadmium (Cd), which is associated with chronic health outcomes including lung cancer, chronic obstructive pulmonary disease, and compromised lung function [20].

Human exposure to particulate matter emitted by road vehicles includes complex mixtures of metals from tires, brakes, wear parts, and resuspended road dust [21].

A research study identified that, across all cities studied, the most significant contribution to potential ecological risk stemmed from lead (Pb) [22]. Pb may also pose a potential health risk, particularly to children. It is imperative to continue efforts toward identifying the primary sources of Pb within urban areas and devising strategies to mitigate the potential adverse effects associated with this metal.

In Slovakia, historical records show that prior to the 1970s, each liter of gasoline contained roughly 0.6 g of lead. This resulted in the emission of approximately 120,000 tons of toxic lead into the atmosphere from vehicle exhausts. However, with the introduction of unleaded petrol in 1985, lead content in vehicular emissions was reduced substantially to approximately 20,000 tons per year. The enduring presence of lead in these emissions can be predominantly attributed to unleaded gasoline, which still retains up to 0.005 g of Pb [23]. Lead contamination also comes from the corrosion of Pb wheel balance weights, and it has resided in the environment for a long time [24]. Lead compounds have been incorporated into tire materials since 1839, when Charles Goodyear, in his pioneering work, heated a blend of natural rubber, sulfur, and white lead, giving birth to the world's first heat-resistant rubber compound. The utilization of lead oxide persisted in tire vulcanization until relatively recently. Additionally, during their lifespan, tires can accumulate lead content from sources such as discarded wheel balance weights and lead oxide pigments employed in road striping [25].

Silica has been designated as a potent carcinogen by authoritative organizations such as the National Institute for Occupational Safety and Health [26], the International Agency for Research on Cancer [27], and the U.S. National Toxicology Program [28]. Among various groups, construction sites, building maintenance activities, and agricultural work are identified as having the greatest susceptibility to silica exposure. Studies have revealed that silica is present in cement dust, making individuals in these sectors particularly vulnerable. This dust exposure has been associated with a range of health concerns, including chronic lung diseases, morbidity, premature birth, endocrine disorders, and infertility. The severity of these effects is contingent on factors such as the duration of exposure, concentration levels, and the individual's susceptibility to silica-related health risks [29].

1.3. Objectives of the Research Study

The objective of this article is to analyze particulate matter (PM) in an area with frequent high traffic from two perspectives: dust deposits and airborne particles. The primary focus is on metal concentrations within dust samples, while the secondary analysis aims to explain the origins of these metals by visualizing PM concentrations generated primarily by vehicular traffic. The samples were taken from the road verge and in a high vegetation area, displaced from the road section by 90 m, in a residential garden.

2. Materials and Methods

To determine metal concentrations, soil samples were obtained through measurement sampling from two distinct areas. The first lot of samples was obtained from the road verge of an area characterized by substantial vehicular activity [30], while the second lot was sampled from 90 m away within a densely covered vegetation area in a residential garden. This investigation was conducted near the city of Timisoara, Romania, on the DN691 road in a residential peri-urban town called Dumbravita. This road faces heavy traffic due to its location on the outskirts of Timisoara and serves as a crucial route, providing access to residential areas, being the main access road to highway A1, and being close to production facilities and logistics hubs. The samples were taken on 29 July 2023, starting next to the pavement (road verge). Sampling was conducted with the help of a laboratory spoon, and the PM was collected in sealed bags.

Sample no. 1 from the road verge is located immediately next to the pavement, while sample no. 7 is 7 m away. The same sampling method was used in the garden area, with sample no. 8 being closer to the main road and sample no. 14 located 7 m further into the garden area. Two sets of dust samples were taken from each position.

The road verge sampling model is shown in Figure 1.

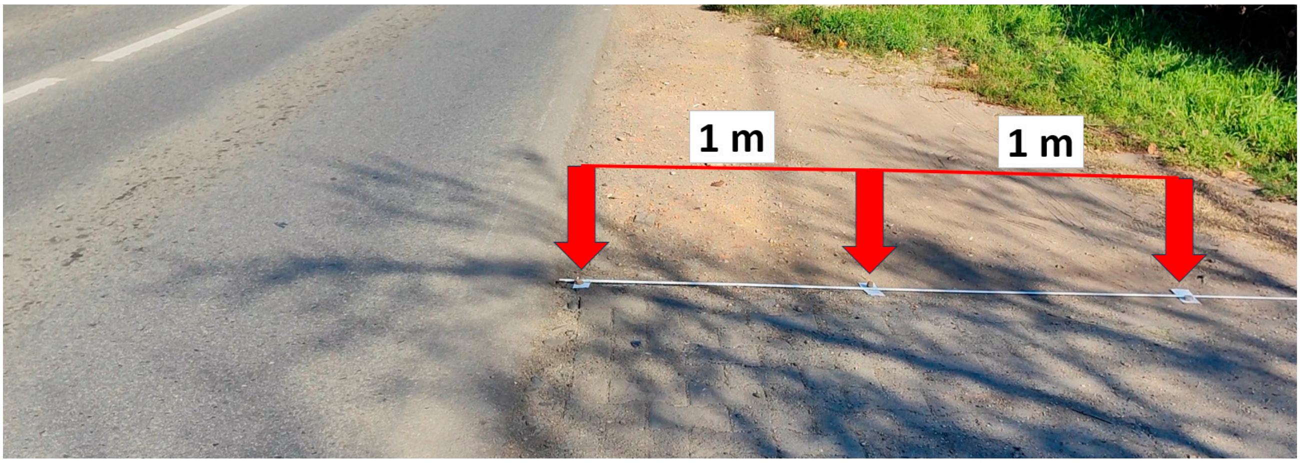


Figure 1. View of the sampling locations for dust particles from the road verge.

Each experiment and sample analysis was carried out using calibrated and metrologically certified equipment, under the university's SR EN ISO/CEI 17025:2018 accredited laboratory (www.mediu.ro, accessed on 30 August 2023).

The soil samples were analyzed with a calibrated electron microscope, which uses energy-dispersive X-ray (EDS) technology (equipment model Quanta FEG 250).

In addition, to explain the origins of these metals, measurements of airborne PM concentrations were carried out using a calibrated spectrometer (equipment model Portable Aerosol Spectrometer model 1.109), which uses light scattering to determine the concentration of particulate matter, allowing a measurement interval of one second.

Assessing the variations in the intensity of light scattered from a suspension or solution provides a means to ascertain particle size. This technique is commonly referred to as dynamic light scattering (DLS), with its primary utility centered on the analysis of nanoparticles [31].

The manufacturer of the spectrometer is GRIMM Aerosol Technik, part of the Durag Group, with its headquarters in Hamburg, Germany.

The spectrometer was placed in two positions: one next to the road verge and the other 90 m away in a garden area of a residential home, in the same position from where the dust sampling was carried out. The exact position is referred to in Figure 2. The duration of each measurement is approximately 2.5 h taken during the middle of the day, 13:00–18:00 interval.

Placing the test equipment and measuring in two different areas should normally indicate a difference in the concentration levels of PM; this is due to the second measurement being performed in an area with dense vegetation, which should block a certain number of particles reaching this area.

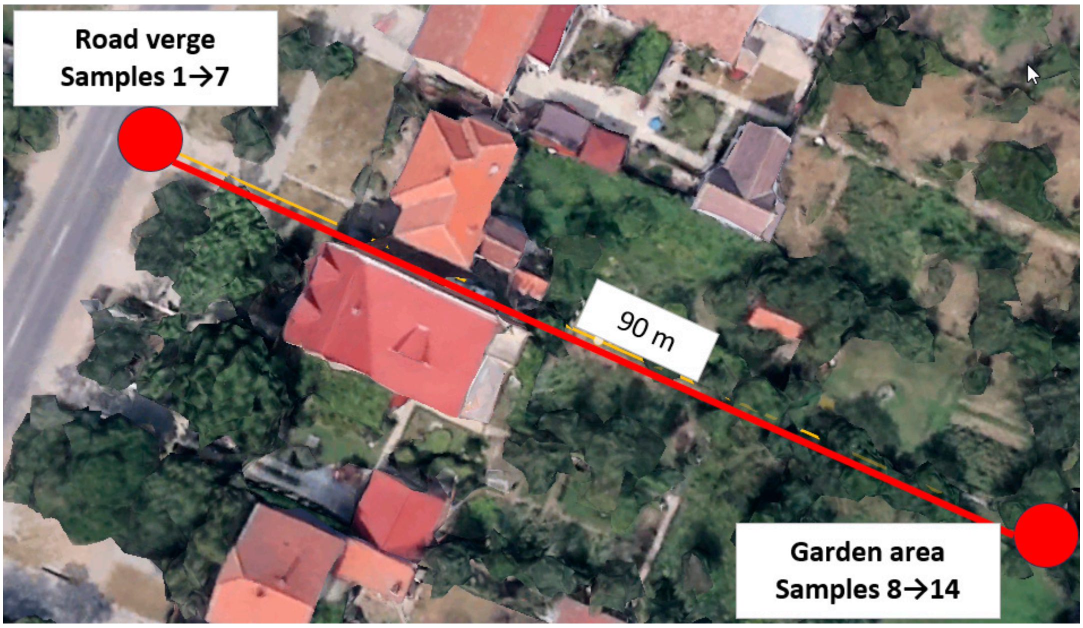


Figure 2. Placement of the spectrometer for sampling within the two measurement episodes.

3. Results and Discussion

The results are split into two sub-sections, with one representing the metal concentration analysis from the dust samples and the other showing the airborne concentration levels of PM.

3.1. Determination of Metal Concentrations from Dust Samples

Metals were found in the dust samples, with a different concentration level between the two areas of sampling.

Analysis of the dust samples taken from the road verge has detected Na (sodium), Mg (magnesium), Al (aluminum), Si (silicon), Pb (lead), K (potassium), Ca (calcium), and Fe (iron) chemical elements in different concentrations, as shown in Figure 3.

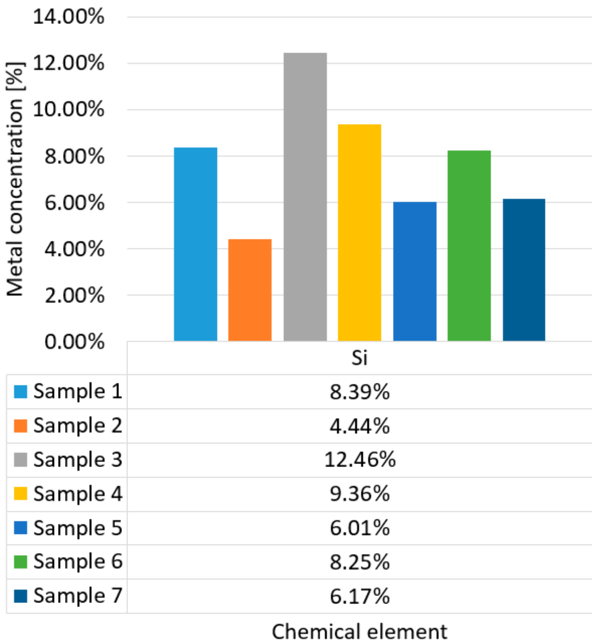
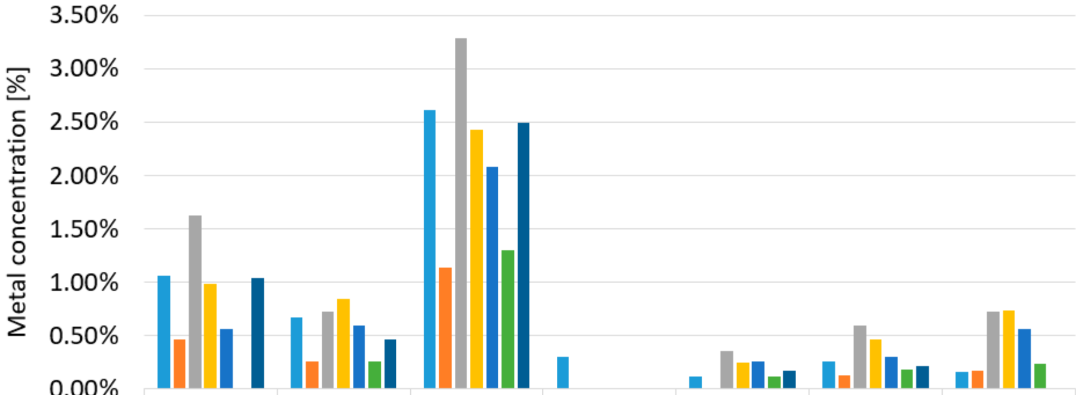


Figure 3. Si concentrations found in the road verge samples.

Not all chemical elements are present in each sample; Pb was detected in only one of the samples, and K was present in six of the seven total samples.

Of the chemical elements present in different concentration across all samples, the highest concentration is of Si, ranging from 4.44% to 12.46% composition (detailed in Figure 3), while the other metal elements present concentrations between 0% and 3.29%, as shown in Figure 4.



	Na	Mg	Al	Pb	K	Ca	Fe
Sample 1	1.06%	0.67%	2.61%	0.30%	0.12%	0.26%	0.16%
Sample 2	0.47%	0.26%	1.14%	0.00%	0.00%	0.13%	0.17%
Sample 3	1.63%	0.73%	3.29%	0.00%	0.36%	0.59%	0.72%
Sample 4	0.99%	0.84%	2.43%	0.00%	0.25%	0.47%	0.74%
Sample 5	0.56%	0.59%	2.08%	0.00%	0.26%	0.30%	0.56%
Sample 6	0.00%	0.26%	1.30%	0.00%	0.12%	0.18%	0.24%
Sample 7	1.04%	0.47%	2.49%	0.00%	0.17%	0.22%	0.00%

Chemical element

Figure 4. Metals present in the analyzed dust samples from the road verge.

Looking to the dust samples taken from the garden area with dense vegetation, the metal concentrations are varied, without any presence of Pb. The rest of the metals have varied concentrations, as shown in Figure 5, but with a reduced concentration.

In one of the samples obtained from the road verge, lead (Pb) was detected, possibly attributable to residual soil deposits. The reasoning is explained in the introduction part of this article, with the literature highlighting how Pb is deposited and why it is found in the soil.

All metals present in the garden area samples are naturally found in soil, with increased concentrations for Al and Si due to their usage as fertilizer compounds in the garden.

An explanation for why Si is found in higher concentrations in the road verge could be trucks and construction vehicles passing through the area. The residential area is constantly growing and developing with new residential homes; therefore, a lot of construction sites are present. Silicon is usually found in dust particles around construction. Dust containing silicon is spread by the tires of vehicles that have passed through areas exposed to construction materials such as cement. Cement dust can be easily transported and spread in different areas. The levels of silica exposure in occupational settings are comprehensively documented and globally estimated. Silica dust is responsible for causing debilitating conditions such as silicosis and lethal lung diseases. Consequently, numerous countries across the globe have established air quality standards tailored to occupational environments, which are focused on regulating the percentage of silica present in the ambient air. A multitude of operations, such as drilling, blasting, crushing, screening, transportation, pulverization, galvanizing, and various metalworking processes, generate significant dust emissions, including the presence of silica in the air [32].

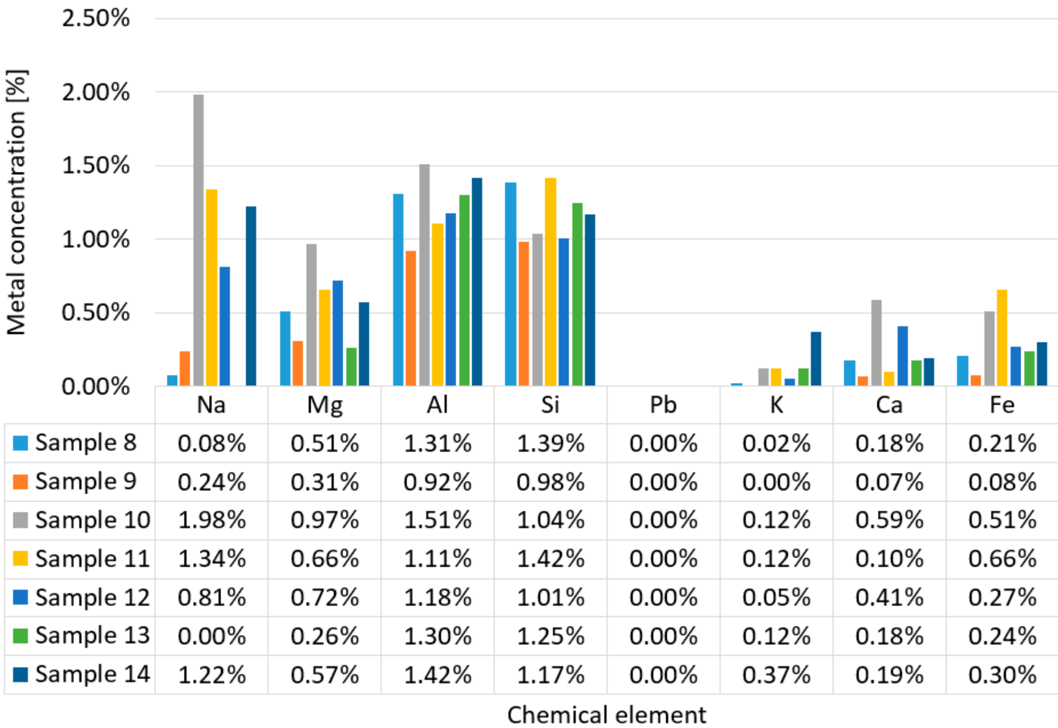


Figure 5. Metals present in the analyzed dust samples from the garden area.

3.2. Determination of PM Concentrations Using DLS Spectrometer

Measurements were taken in the same way to compare the road verge with the garden. The duration of each measurement was approximately 2 h. Each measurement was taken at an interval of 6 sec, determining the concentration levels for PM1, PM2.5, and PM10.

The sizes of PM pose a threat to human health, being able to pass through the several safety mechanisms in the human respiratory system. PM10 particles are inhalable-sized and able to pass through the nose hair; PM2.5 particles are thoracic-sized, passing through the throat mucus and the lungs; and PM1 particles are alveolar-sized, with the ability to reach and pass the alveoli into the blood stream.

Temperatures recorded on 29 July 2023 during that measurement episode were at a maximum of 37 °C and an average of 28 °C. Wind speed was at an average of 10 km/h, with a wind direction predominantly from E to W and S to N, blowing toward the nozzle of the spectrometer [33].

Road verge measurements have determined different concentrations of PM, as shown in Table 1.

Table 1. Values of PM_1, $PM_{2.5}$, and PM_{10} concentrations measured using the DLS spectrometer taken from the road verge.

Variable	PM_1 (µg/m^3)	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)
Minimum	5.4	6.1	6.1
Maximum	68.6	143	889.8
Mean	7.9	10.7	27.1

The logarithmic dispersion of PM concentrations on the entire measurement episode from the road verge is shown in Figure 6.

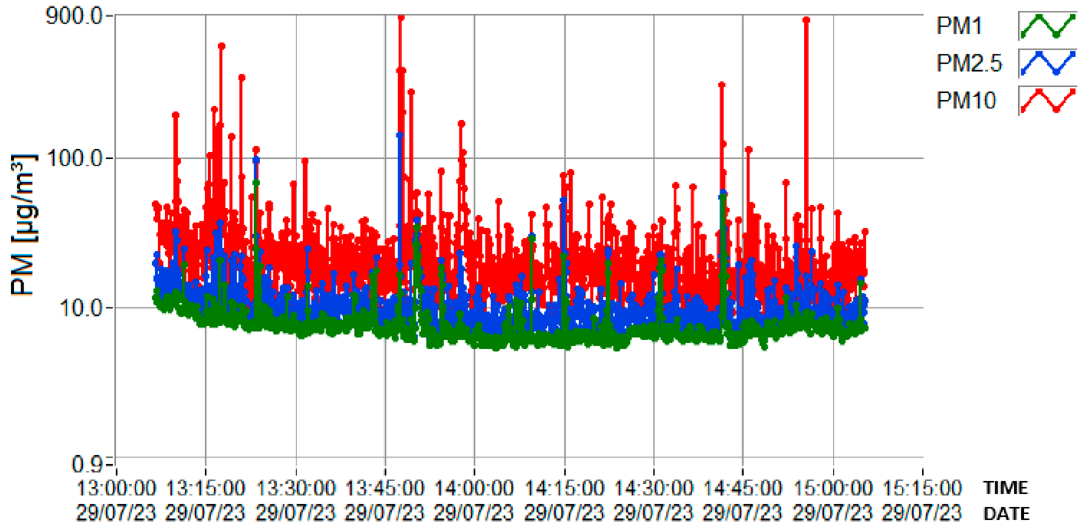


Figure 6. Logarithmic dispersion of PM concentrations taken from the road verge.

The garden section concentrations of PM are shown in Table 2.

Table 2. Values of PM_1, $PM_{2.5}$, and PM_{10} concentrations measured using the DLS spectrometer taken from the garden area.

Variable	PM_1 (µg/m^3)	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)
Minimum	7.8	8.1	8.4
Maximum	16.4	27.7	52.3
Mean	11.7	13.3	20.1

The logarithmic dispersion of PM concentrations on the entire measurement episode from the garden area is shown in Figure 7.

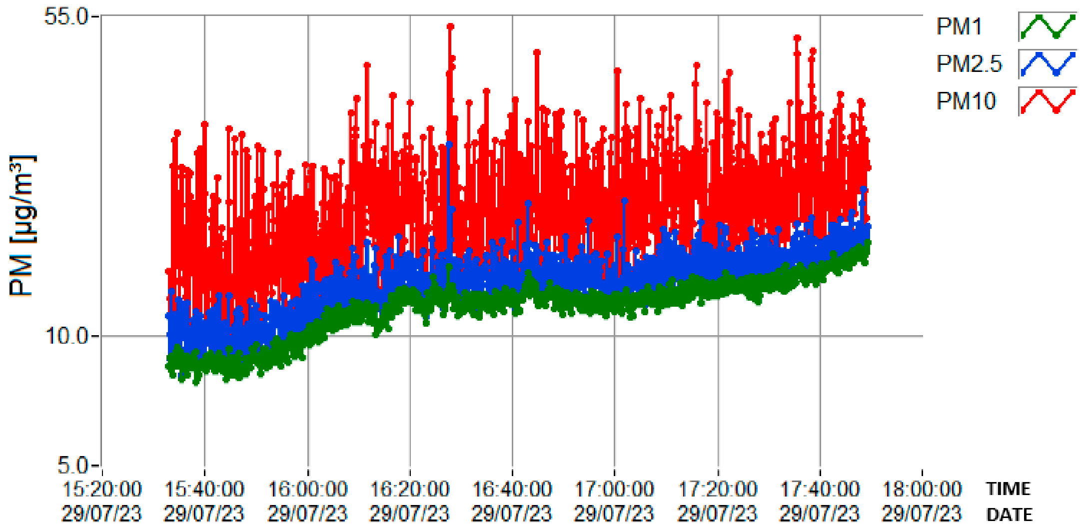


Figure 7. Logarithmic dispersion of PM concentrations taken from the garden area.

Looking at the maximum concentration levels detected, it is evident that along the road verge, concentrations of PM are considerably higher than in the garden area with dense vegetation. The biggest difference could be recognized in PM10, which shows values of 889.8 µg/m^3 for the road verge versus 52.3 µg/m^3 for the garden area.

Based on these differences, it can be deduced that a dense vegetation area is helpful in blocking quite a high amount of PM concentrations.

In accordance with Romanian legislation, the permissible threshold for PM10 concentration is established at 40 µg/m^3 annually, accompanied by a daily threshold of 50 µg/m^3. This daily limit must not be surpassed for a duration exceeding 35 days in any given year [34]. On the other hand, concerning PM2.5, the regulations outlined in European Union Directive 2008/50/EC dictate an annual average of 20 µg/m^3 [35], a standard to which Romanian Law does not presently provide corresponding limitations. It is worth noting that neither Romanian Law nor the directives within the European Union framework impose any specific restrictions on PM1.

4. Conclusions

This research analyzed the presence of several metals taken from dust samples from the road verge and from a garden area with dense vegetation. Based on the results, a high concentration of Si can be found in the dust samples from the road verge, which is usually due to construction site activity. Pb is also found in one of the samples from road verge.

Measurements were taken using a DLS spectrometer to determine the concentrations of airborne PM, which resulted in a significant difference between the two measurement positions of the road verge versus the garden area. Dense vegetation can block a high amount of airborne PM. The advantages of using the DLS spectrometer measurement technique are the ability to capture, in a very small time frame (every 6 s), PM concentrations of different sizes that pose a threat to human health (inhalable-, alveolar-, and thoracic-sized particles). The disadvantage of using the DLS is the inability to physically store PM samples; therefore, the usage of complementary measurement methods and equipment (i.e., electron microscopes) is needed.

Health effects of various metals and elements found in PM were detailed with specific literature references.

Nevertheless, in both measurement positions, the limit for PM exceeded the law-binding values given by the EU and Romanian laws and norms.

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