

INDOOR CONCENTRATION AND COMPOSITION OF FINE PARTICULATE MATTER (PM2.5) NEAR AN INTENSE CIRCULATED ROAD IN AN INDUSTRIAL CITY

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ABSTRACT

The purpose of the present work is to present results from a measuring campaign during February-March 2020, in Galati city, Romania, aiming the concentration of fine particulate matter $(PM_{2.5})$ in air and their heavy metal concentrations, then comparing the results with the air quality determined by the national monitoring system from the same city. Results show considerable differences concerning the air quality measured in this study compared with measurements of the national monitoring system that consist in four stations placed across the city. While values recorded in this study exceeded, in some situations, the maximum target from $PM_{2.5}$, the reports from the national monitoring system presented a good air quality, using a colour- and number-coding (maximum level 4 out of 6 was reported). Heavy metal concentrations of the fine particulate matters collected in this study was compared with other studies across the world, high Fe and Zn values being registered in agglomerated and industrialized cities, including the city considered in the present study, while in a study conducted in Beijing, China most higher values between all analysed heavy metals were recorded.

KEYWORDS: air quality, fine particulate maters, X-ray fluorescence

1. Introduction

The overall environmental situation in the world made air, water and soil quality monitoring to become compulsory in some situations. Air quality monitoring became compulsory in Romania, according to European Directives, for all urban agglomerations surpassing 100,000 inhabitants [1]. The pollutants taken into consideration and the way the air quality status is presented to the population was also standardized and included into Romanian legislation [2].

During air quality monitoring, two types of particulate matter (PM) dimensions are usually taken into consideration: $PM_{2.5}$ and PM_{10} , the later one being more frequently tracked, at least according to the Romanian legislation [2, 3]. This might be since this type of particle matter analysis also include the other, finer and more dangerous, PM dimensions: $PM_{2.5}$. The $PM_{2.5}$ quantitative analyses represent the determination of cumulative particulate matters mass for particle fraction with a 50% aerodynamic cutoff diameter of 2.5 µm in a known volume of analyzed atmospheric air [4-6]. The effect of this type of

pollutant is well documented [7-8] and works are still emerging in the specialized literature, especially in Asia [9-12], where multiple great human agglomerations creates the premises [13] for extremely high values of particulate matters in the atmosphere (e.g.: a mean concentration of 102.45 μ g/m³ in Beijing, China, during 2015-2016 period, for PM_{2.5}) [14].

This type of pollutant was chosen for the present study since the finer share of particulate matters is considered most dangerous for the human health and although permanent monitoring stations already exist, articles from Eastern Europe are scarce and qualitative analysis of these particulates are even more so. While, as mentioned above, there are some hints regarding the effect of PM_{2.5} on human health, the corroboration of qualitative analyses and health effect was not identified in the specialized literature and the possibility to do just that might emerge once a sufficient amount of data will be at hand. In this regard, this paper aims to present a comparation of air quality resulted from the local monitoring system and that registered in a residential apartment focused on the quantitative analysis of PM_{2.5}. Also, qualitative



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analysis (heavy metals concentration) was addressed, obtained data being compared with other studies around the world, most of them also focused on indoor $PM_{2.5}$ determination.

2. Materials and methods

The sampling campaign took place in Galati (an approx. 250,000 inhabitants city in south-east of Romania), in a building facing a four-line road with a fairly high traffic (Latitude: 45.433650, Longitude: 28.028543), during February and March 2020. The sampler was placed intermittently (24 hours for each filter) in a living room and inside its enclosed balcony (at all times with both balcony and living room windows being tilt-opened) of a residential apartment at the third floor. Against the pollution and noise from the road, as a green buffer (although during the sampling period the trees were without leaves), the building in discussion has a line of trees high enough to reach the fourth floor, situated between the road and the sidewalk near the building. The sampler was placed each time on the floor with its filter holder being situated at a height of 1.2 m.

2.1. Gravimetric analysis

In the present study, the same instruments and methodology as in [15] was used. Thus, for PM_{2.5} collection an Automated Aerosol Sampling Device, type ISAP 1050e, was utilized (Figure 1-left). The flow rate of this device was equal to $2.3 \text{ m}^3/\text{h}$. Particulate matters were collected on a glass microfiber with 45 mm in diameter, a 0.30 mm in thickness and 0.7 µm in pores size (Figure 1-right), the support holder used this time being a specially PM_{2.5} type one (Figure 1-middle). The filter was placed in the holder, between a rubber garniture and a metallic made mesh as a support. Before and after the aerosols collection, the filter was weighted using an analytical balance (type ALT 220-4NM, from KERN). The particulate matters collection time for each measurement was 24 hours, each time a new filter being used. The quantity of PM_{2.5}, expressed in $\mu g/m^3$, for one analysis was calculated based on the overall particles mass (gravimetrically analyzed), the volume of air filtered by the sampling device and the functioning time of this device (both values automatically calculated by the sampler and presented in a report and downloaded from the sampling device after each 24 hour functioning time).



Fig. 1. The Automated Aerosol Sampling Device, type ISAP 1050e, used for $PM_{2.5}$ collection (left) and the support holder (middle) for the glass microfiber filter (right-up), blackened by particulate matters after 24-hours utilization (right-down)

2.2. Qualitative analysis of fine particulate matters

Before and after a 24-hour functioning of the sampling device, the filter was placed/extracted

into/from the holder and weighted. Also, before and after the 24-hour functioning of the sampler, the side chosen to accumulate particulate matters was analyzed to determine the elemental composition using an INNOV-X type (α A-4000 series) X-ray fluorescence (XRF) spectrometer with an X-ray tube



with acceleration tension of 40 kV, a Si-PiN<280 eV diode detector (thermoelectrically cooled), with 5.95 eV/K- α line. The values of XRF analyses represents an average of six separate readings, each reading being done on different surface of the same filter side. This way, most of the filter surface exposed to the intake air was analyzed before and after the sampling, increasing the obtained data solidity. As in [15], the concentration of heavy metals in retained PM_{2.5}

where:

HMC - concentration of a certain heavy metal, [ng/m³];

 Av_{UF} - average value concentration of a certain heavy metal for a used filter, [µg/cm²];

 Av_{BF} - average value concentration of a certain heavy metal for a blank filter, [µg/cm²];

EFA - exposed filter area (12.56 cm^2) ;

SV - air sample volume (55.2 m³).

The values obtained after performing this analysis were then compared with those from the available literature, also aiming $PM_{2.5}$ qualitative measurements. The elements detected in this study (Ti, Ba, Cr, Mn, Fe, Zn, Rb and Sr) might not be mentioned in the legislation regarding their maximum permitted values, instead a comparison with other studies might offer an insight related to the fine particulate matters concentration from the elemental point of view.

3. Results and discussions

Results of this work, regarding the PM_{2.5} concentration, were placed in contrast with results from the national monitoring system. The national monitoring system has 4 stations placed inside Galati city and the results are presented on the official website for each measured pollutant [17]. Also, to ease public information, an electric panel placed in a visible place inside the city presents in a color- and number-coded way the situation of air quality. Monthly reports are also available on the official website [18] and those issued for February and March periods were used for comparison in this study.

Since most of heavy metals concentrations in air are not regulated, a comparison was possible only with the available literature and various studies from numerous countries from different continents were selected. samples was calculated as described in [16]. Thus, the average value mentioned above (expressed in $\mu g/cm^2$) was multiplied with the exposed filter area (12.56 cm², smaller than the actual filter area of 15.89 cm²), subtracting the value obtained the same way for the blank filter, then dividing by the air sample volume (55.2 m³) and then multiplying with 1000 so the final data to be expressed in ng/m^3 (Equation 1).

$$HMC = \left(\frac{(Av_{UF} - Av_{BF}) \times EFA}{SV}\right) \times 1000, [ng/m^3]$$
(1)

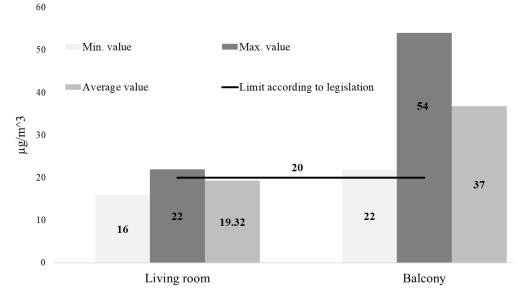
3.1. Evolution of PM_{2.5} concentration in the analyzed air samples

Results regarding the PM_{2.5} concentration are presented in Figure 2, separately presented for living room and balcony sampling. Also, according to the national legislation, starting from 1st January 2020, the maximum annual exposure must not exceed 20 $\mu g/m^3$, and this value is represented as a constant in Figure 2. As expected, values inside the living room (average of 19.32 μ g/m³) are lower compared to those from the balcony (average of $37 \ \mu g/m^3$). Nevertheless, it is worth mentioning that although the sampling from living room took place in a space separated from the outdoor atmosphere by two rounds of tilted windows, the maximum value recorded for this type of particle matters was 22 $\mu g/m^3$ and the minimum was not far behind. Furthermore, all values inside the balcony, thus separated only by one tilted window from the outside atmosphere, exceeded the annual maximum limit of 20 µg/m³. The highest value, of 54 μ g/m³, represents almost three time the admissible value and the average for the balcony almost double. It must be mentioned that the weather was also monitored and no major differences were recorded. For the February-March 2020, the temperature varied between 5 and 20 °C, very few and brief showers, and the relative humidity varied between 45 and 81%.

For the same period, the reports for Galati city issued by the national agency presents a good air quality, using the beforementioned coding system. This coding system present 6 levels, based on each measured pollutant concentrations. If any of the five pollutants (SO₂, NO₂, O₃, CO and PM₁₀) measured by the monitoring station reaches a high level, the overall air quality is considered to be of that level. For the considered period, the air quality level varied between 1 and 3 for all four monitoring stations in February [19] and between 1 and 4 for all four monitoring stations in March [20], meaning that no exceeding of maximum values for PM₁₀ was recorded. Although the monitoring stations measure PM₁₀ and the present study presents values for PM_{2.5},



the overall quality of air samples might be compared since the PM_{10} fraction also incorporate fine particulate matters. However, as presented in [21], various methods or instrumentation used for measurements and different people or places involved, represent a big factor that might influence the outcome, especially regarding the fine fraction of the particulate matters. Also, in [22] data from a monitoring station in Galati city was used to demonstrate the dependence of particulate matter concentration from air on wind speed. All of these being considered, it can be stated that the air quality monitoring should continue in agglomerated cities and the national monitoring system could reevaluate the positioning of some monitoring stations or their supplementation, so that relevant data to create the premises for future actions in pollution mitigation. The city considered in this study is an industrial one, a steel company and a naval yard flanking it from west and east respectively. Also, a large number of vehicles (approx. 216,000, of all types [23]) ads as the major source of PM_{2.5} pollution especially inside the city and mostly for locations near roads with high traffic, like the one selected for this study. More detailed and relevant information regarding the air pollution could in the end be the starting point for measures needed to obtain a less polluted air and consequently less pollution related diseases.



*Fig. 2. Results of PM*_{2.5} *concentration in air: minimum, maximum and average for Living room and Balcony measurements, compared with the limit according to Romanian legislation*

3.2. Heavy metal concentration in collected PM_{2.5}

Particulate matters collected from the air samples contain different organic compounds or heavy metals that might negatively impact health population. Different studies around the world were focused on quantifying some of the possible heavy metals present in PM_{2.5}. Some results are offered in Table 1, and the majority of studies present results from indoor measurements. Also, Table 1 contains results from the present study for the living-room and for the balcony measurements. As expected, values of all elements considered were higher for balcony samples, except for Cr. One of the many possible explanations, for this unexpected result, might be the intermittence of sampling, the Automated Aerosol moved from Sampling Device being one measurement space to the other in different days. To

overcome this drawback, a second device, running in tandem, could be used in future measurement campaigns. Nevertheless, compared to the former study conducted in Galati, in a different outdoor site [15], the values for Cr, Mn, Zn, Fe are comparable, lower for the present study, as expected, instead high values for Fe and Zn are again registered.

High values for Zn and Fe are also present in other studies conducted in cities with heavy industry, the highest value for Fe (1767,9 ng/m³) being reported in Rooty Hill in Australia, and the highest value for Zn (950 ng/m³) being reported in Beijing in China, while the lowest value for Fe (84.06 ng/m³) was registered in the present study for living room measurements and the lowest value for Zn (34 ng/m³) was registered in Córdoba, Argentina. High numbers were also registered for Ba, although fewer studies measured this type of heavy element. Again, for Ba, Beijing (China) registered the highest value (523,65



ng/m³), this city also presenting highest values, from all compared studies, for Mn (85 ng/m³) and Sr (60 ng/m³), while for Ti (167.5 ng/m³) and Cr (121.7 ng/m³) the highest values were registered in Istanbul in Turkey and for Rb (3 ng/m³) in Cairo, Egypt. It is expected that high concentrations of heavy metals to be present in populous cities and even higher in industrialized ones, this is why this type of agglomerations should be better monitored from the air pollution point of view. From data presented in this paper it can be observed, when compared with the air quality national monitoring system, that big differences might occur between different areas of the same city, this is why a greater involvement in this respect and the subsequent measures should be applied in the near future.

| (ng/m^2) | | | | | | | | |
|-----------------------------------------------|-------|--------|-------|-------|---------|--------|-------|-------|
| City (Country) | Ti | Ba | Cr | Mn | Fe | Zn | Rb | Sr |
| This study (balcony), Galați (Romania) | 22.12 | 157.88 | 4.80 | 71.16 | 415.25 | 574.27 | 1.64 | 17.69 |
| This study (living room), Galați (Romania) | 22.62 | 106.18 | 29.83 | 12.64 | 84.06 | 437.75 | 1.39 | 16.81 |
| Cairo (Egypt) [24] | 48 | NA | NA | 12 | 594 | 112 | 3 | 13 |
| Beijing (China) [14] | NA | 523.65 | 34.33 | 85 | NA | 950 | NA | 60 |
| Xian (China) [25] | 49 | NA | 5 | 50 | 806 | 587 | NA | 7 |
| Chongqing (China) [25] | 34 | NA | 4 | 41 | 408 | 152 | NA | 1 |
| Córdoba, (Argentina) [26] | 12 | ND | 4 | 14 | 325 | 34 | NA | NA |
| Thessaloniki (Greece) [27] | 45 | 125 | 23 | 35 | 426 | 110 | NA | 17 |
| Oporto (Portugal) [28] | NA | 2.65 | 4.01 | 3.54 | NA | 48.1 | 0.702 | 1.21 |
| Shiprock, NM (USA) [29] | 3.44 | 1.61 | NA | 0.93 | 44.7 | 1.22 | 0.1 | 0.37 |
| Istanbul (Turkey) [30] | 167.5 | 241.9 | 121.7 | 42.1 | 117.3 | 384.7 | 1.05 | 10 |
| Jeddah (Saudi Arabia) [31] | 55 | 34 | 2.1 | 19 | 590 | 41 | 1.2 | 4 |
| Monterrey (Mexico) [32] | NA | NA | 3.8 | 29.78 | 1026.18 | 39.19 | NA | NA |
| Rooty Hill (Australia) [33] | 8.9 | NA | 5.5 | 47.2 | 1767.9 | 284.4 | NA | NA |

Table 2. Mean concentration of heavy elements in $PM_{2.5}$ from this study, compared to other studies (ng/m^3)

4. Conclusions

As demonstrated by a large number of researches, the fine particulate matter in the breathable air is a major concern on public health. This is why the first obvious step is quantifying the extent of pollution with this type of pollutant. Numerous independent parties (e.g.: [34]) already started the monitoring of air in some big cities around the world and some surprising data already occurred, revealing that sometimes, the existing national monitoring system is unable to present the real extent of air pollution. Complementary to those situations, the present study demonstrates again this possibility, by comparing data regarding fine particulate matter concentration from an indoor site with data regarding the air quality from four monitoring stations of the national system during the same period (February-March 2020). While in the present study the legislative limit was exceeded by the measurements inside a balcony (a mean value of almost two times being registered), and the measurements inside a living-room almost reached the maximum admissible value, the four existing monitoring stations in the same city presented a maximum level of 4 out of 6 for the air quality. Although different types of measurement techniques and other influencing factors

could be a reason for these differences, it is clear that reevaluation of monitoring sites positioning or supplementation could be a possibility worth considering. Meanwhile, independent measurements will continue, and the present study will be followed by others, monitoring particulate matters at the same time in different sites being one of the goals. Also, measuring this type of pollutant at the same time in the same site and at different heights might shed some light regarding the dispersion of particulate matters inside artificial canyons formed by roads flanked by high buildings.

Measurements of $PM_{2.5}$ concentration were completed by heavy metal concentration analyses. Data obtained this way were compared with results of other studies worldwide, most of them dealing with indoor $PM_{2.5}$ measurements. Of all heavy metals considered, highest values were registered for Fe and Zn in this study, compared with a former study conducted in an outdoor site from Galati city. Similar situations were also registered for all the other studies, higher values, as expected, being recorded in agglomerated and industrialized cities, the study conducted in Beijing being the one presenting the highest values for 4 out of 8 heavy metals considered (Ti, Ba, Cr, Mn, Fe, Zn, Rb and Sr). Results from the present study could be further supplemented in the



future with data from other type of analysis methodologies, such as X-ray diffraction, for PM_{2.5} mineralogical composition and scanning electron microscopy, for morphologic analysis purposes.

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