IMPROVEMENT OF AIR QUALITY MANAGEMENT STRATEGY BY EVALUATION OF URBAN POLLUTION

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Abstract. *Air quality management strategy (AQMS), designed on the original results of air pollution research, is significant and efficient, and can be effectively employed in managing acceptable urban air quality. The AQM practices are specific to a particular region needs and requirements, based on a regulatory management framework. The first objective of this review is focused on the evaluation of sources of particulate matter pollution in atmosphere of different areas in Cluj-Napoca, Transylvania, Romania, using the top appropriate techniques. The second objective is to figure out a prospective strategy for the AQM improvement based on the physical and chemical data obtained from the investigation of samples collected from the areas of interest.*

Keywords: particulate matters, pollution, atmosphere, AFM, XRD, TEM, SEM.

1. Introduction

The result of environment manifestations is the formation of new phases in the atmosphere. These aspects are investigated in order to understand and discover new (related) phenomena of interest [1-5]. Street dust (SD) is a complex of particulate matter (PM), due to the constructive or destructive phenomena happened in the nature. Street dust presents environmental concern and health risks for the citizens due to its high content of impurities and polluting factors [2]. The main street dust sources are natural (e.g., soil decay, volcanoes, space) [3-5]

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and anthropogenic one (transports, industrial activity, house hold duties, smoking) [6]. The air quality [7, 8], like PM10, PM2.5, and PM1 [9, 10], could be modified by them.

According to the composition, street atmospheric pollutants can be classified as: **allergen** (pollen, spores, and fungi) from the vegetal reign; **bacterial** (bacteria from the nose secretions and other animal emissions), **residual** emissions (industrial wastes). **Irritant** emissions are mainly of gaseous nature, originated in the industrial and combustion chemical processes [5, 11].

Atmospheric suspensions are solid and liquid particles, having a particular size and chemical composition, in the air [3, 12, 13]. Some of them could be observed by the human eye, (sand and dust, formed by strong air currents), or not (ashes, soot of fine particles). There could be bacteria, viruses, and other pathogens, which are able to increase the environmental hazard. Such fines particles could be observed by physical and chemical methods, like microscopy and spectrometry. The evaluation of urban pollution is a very important goal, leading to an improvement of air quality management strategy (AQMS). The main classes of atmospheric suspensions are described further.

PM10 are the particles suspended in the atmosphere, having the aerodynamic diameter ≤ 10μm [14-16]. Its sources depend on the close relation between environment and weather, as natural factor, and human activities as anthropogenic factor [17–20]. The maximum accepted level of PM10 is 50 $\mu g/m^3$. The limit excesses should not happened more than 7 times per year, according to US and UE Environment Protection Agency from 1st January 2010 [21, 22]. Although, there are no limitations for the dust amount present in the street, which is a major cause of PM10, the PM10 limits are strongly prescribed and respected in UE [23].

PM2.5. The aerodynamic diameter „d_{ae}" is ≤ 2.5 μm [24-26], and could last long in the atmosphere due to their buoyancy. Moreover, it could be transported for long distances by the air currents, sometimes several kilometers [27].

The sources of PM2.5 could be primary and secondary. The primary sources emit directly particles into the atmosphere and secondary sources release particles via chemical or physical process. Both sources could have natural and anthropogenic components like: minerals, metal fractions, carbon, organic matter, or biologic particles [28]. The maximum accepted limit is slightly lower in US than in UE, perhaps due to their more enhanced monitoring features displayed in the field. The UE target for PM2.5 is of 20 $\mu g/m^3$ by 2020 [29-31].

PM1 has aerodynamic diameter of 1 μm and below [32-35]. Such particles often belong to the secondary sources like biomass, fuel burning, and industrial emission [36-38]. Primary sources are also able to form PM1 by submicron and nano-particles present in the street dust like quartz, kaolinite, and muscovite.

Laboratory analysis of PM10 and PM2.5 often evidenced submicron particles which are susceptible to form a new category of particulate matter suspended into the atmosphere called PM1.

Particulate matter - mainly the micrometer range - presented in the atmosphere could be easily inhaled. You can feel the dust passing through the mouth in a windy weather. PM from 10 to 1, the last much worse, cannot be felt as dust like. They simply get inside the body with each breath. The nose mucosa catches a lot of PM10 and fractions of PM2.5, small particles, especially sub-micrometer and nano-particles are able to get into the lungs and penetrate the membranes of pulmonary alveoli [39-41]. The investigation of environmental particulate matter is very important for a proper air quality management. The best physical and chemical characterization of such samples is given by several methods like: atomic force microscopy (AFM) [42, 43]; X-ray diffraction (XRD); mineralogical microscopy [44]; scanning electron microscopy (SEM); SEM coupled with elemental analysis, EDX, (SEM-EDX); transmission electron microscopy (TEM); Fourier transformed infrared spectroscopy (FTIR). AFM is the most powerful tool for the nanostructures investigation from simple nano-particles to a wide variety of combinations such as: protein nanostructures [45, 4 6], phospholipid domains [47-49], human erythrocyte membrane [50], and collagen fiber [51, 52], collagen porous scaffolds [53], starch granules [54], gold and silver nano-particles functionalized with diverse biomolecules [55-68], and nano-particles of hydroxiapatite [69-78].

The AQM practices are specific to a particular region needs and requirements, based on a regulatory management framework.

2. Major sources of particulate matters

The main objective of this paper is focused on the evaluation of particulate matter pollution in atmosphere sources of different regions, rationally selected in Cluj-Napoca, Transylvania, Romania using the top appropriate techniques.

The clay soil contains small and very small particles of the clay mineral class: silicates having lamellar structure (phyllosilicate mineral class). Muscovite and kaolinite are the most often found clays in Cluj-Napoca on large areas. We could mention few representative sites like: Tăietura Turcului Hill, Cetăţuia Hill and Sf. Gheorghe Hill. The most representative is the XRD pattern presented in Figure 1. The well-developed peaks belong to muscovite and kaolinite proves a great amount of clay is present. Quartz and calcite accompany them from sedimentary sources.

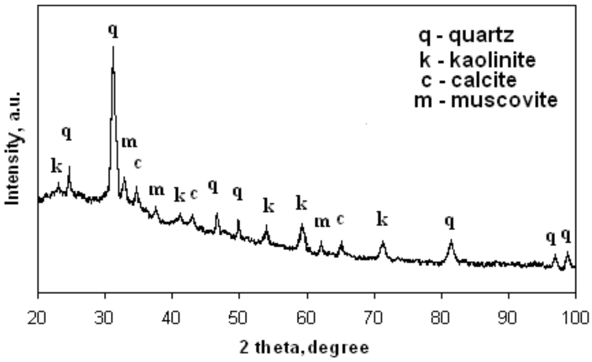


Fig. 1. XRD pattern for clay ground sample [5].

Sands are formed of particles with a wide range of sizes and shapes by rocks disintegration. Quartz is the most common one and can be found mixed with clay. All sand particles are susceptible to be lifted in the atmosphere in proper environmental condition; sands represent a major source for street dust and a major environmental risk.

Marble nanoerosion could conduct to some particulate matter pollution due to the surface degradation. It is one of the most precious construction material [79, 80], often used for building decorations and statues. Acid rain, caused by industrial pollution, may harm marble ornaments in a very destructive manner. Calcium sulphate and calcium nitrate are found to be the most important reaction products, which form refined powders in a dry state. Atomic force microscopy, AFM [81, 82] revealed the erosion structure of the marble exposed to a moderate acid rain of pH 4 for about several weeks. Two stages of nano erosion are evidenced [81]. The first stage affects the inside structure of calcite grain, inducing a nano erosion promotion at an exposure from 0 to 6 days. The transition to the second stage is related to the propagation of nano erosion to the grain borders, very pronounced on day 6. At this stage the marble ornaments are seriously damaged. The second stage corresponds to the massive erosion of the surface at day 24, with irremediable damage to the marble ornaments.

Silicates fragmentation. Street dust collected in Cluj-Napoca contains silicates particle. XRD analysis evidenced mainly quartz, kaolinite, and muscovite (e.g. clay), which belong to silicates. SEM-EDX analysis confirms the XRD results, establishing connections between particles shape and their composition. The identified quartz nano-particles have 90 nm diameters and are surrounded by small clay nano-particles which have the diameter between 40 and 60 nm. Quartz particles are tougher due to Si-O bonds in the hexagonal lattice, meanwhile clay features layers of SiO_4 tetrahedrons stacked into a fold by Si-O-Al bonds which are less strong than Si-O bonds, Figure 2. These arrangements of silicate particles explain how the dynamics in the urban environment causes an intensive dust fragmentation, developed on the weaker crystallographic planes. The fact is sustained by the crystallographic calculation performed on the XRD patterns, where the cleavage planes are observed (e.g. (002) planes). Furthermore, silicate nano-particles were clearly evidenced by AFM and TEM images on the street dust samples made by adsorption from the dust aqueous dispersion. The floating particles collected from the atmosphere contain the same particles observed in the street dust, mainly the quartz and clay nano-particles.

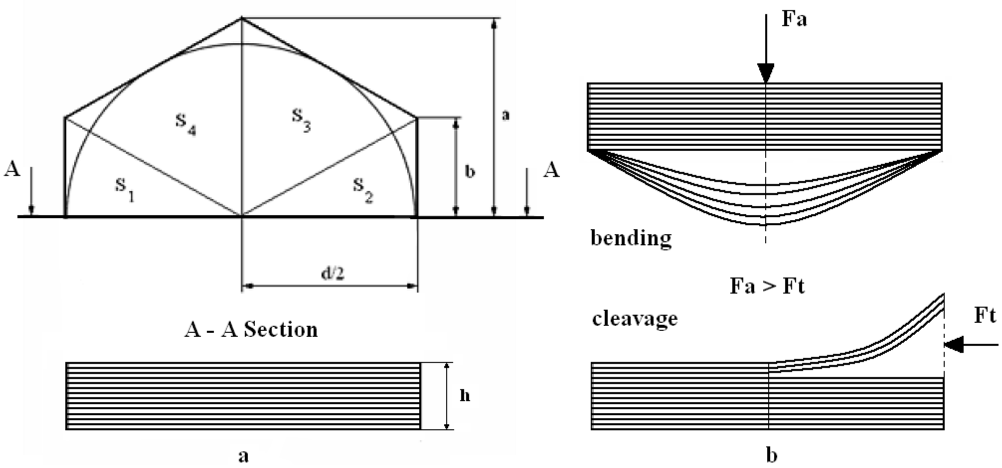


Fig. 2. Clay particle model: a) geometrical shape and
b) external forces acting on the clay particle [5, 93].

The quartz and clay particle fragmentation mechanism is proved by microscopic investigation of SD dispersion in deionized water. TEM images are presented in Figure 3. PM1 is a critical step among PM emissions with maximum diameter of 1μm [9-11]. Several PM1 particles were observed in SD aqueous dispersion. One of them is situated on the bottom of TEM image, Figure 3a. This is a large one, having 600 nm diameters. The particle has connected to the upper side 3 branches of fragmented clay nanoparticles. Their diameter is situated around 40 nm and feature a low thickness since it appears semi-transparent in the TEM beam.

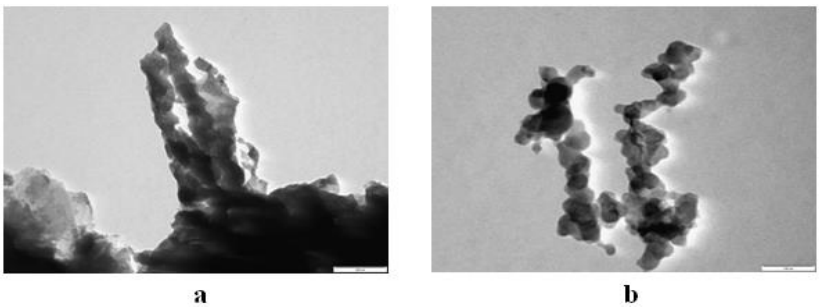


Fig. 3. TEM images proving street dust particles fragmentation until nanostructure level:
a) clay and quartz submicron particles and b) clay nano-particles [5].

Beneath these two PM1 particles appear more fragmented ones with diameters ranging from 40 nm to 200 nm. It is a wide domain of submicron dimensions. Such particles are observed better at high magnification in Figure 3b. A well nano-structured film is formed: quartz nano-particles have around 90 nm and feature a dark aspect due to their spherical shape. Clay particles are smaller around 40 nm diameter and exhibit a light aspect due to their low thickness, and surround quartz particles [93].

The increasing of PM10 and PM2.5 in the cold seasons is strongly related to the efficacy of silicates fragmentation favored by presence of antiskid material, which acts like milling bodies. The intensive fragmentation at low particle size correlated with intense traffic registered in some days (one day per month) leads to values of PM2.5 which exceed the limit. It could be an environmental concern because the appearance of a potential health risk, which could be diminished by a better street dust management.

3. Organization of micro and nano-particles from street dust

Particulate matters found in the street dust are very dangerous and affect walking people, in direct contact with such powder emissions. Thus, intensive physical and chemical analysis of street dusts is required.

Dust from Dâmboviţei Street. Dâmboviţei street is situated in Mărăşti neighborhood. Several main industrial facilities are situated in the close proximity of this street. Many of these companies have metallurgical profile, so there is a high possibility to release ferrous compounds in the atmosphere. The eastern road access in Cluj-Napoca is situated in the proximity of Dâmboviţei street and also a high amount of traffic related particles could occur into the area.

The XRD spectrum in Figure 4 features: quartz is the dominant mineral, followed by clay mixture of muscovite and kaolinite, calcium carbonate crystallized as calcite and at last iron hydroxide. Both crystalline state of iron hydroxide were found: lepidocrocite and goethite. Quartz and lepidocrocite are natural components very often found in common soils [82], but in this case the presence of lepidocrocite is caused by anthropogenic sources like rust from unprotected metallic structures exposed to open environment, rust form car chassis [83].

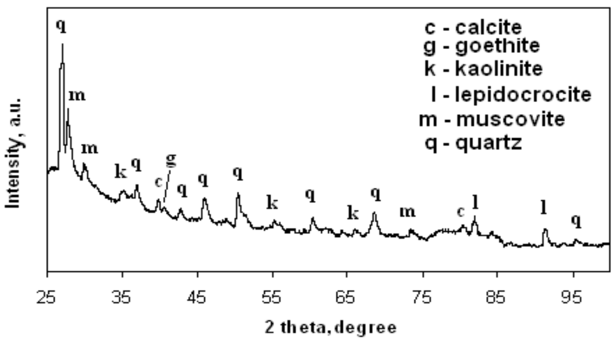


Fig. 4. XRD pattern for street dust sample from Dâmboviţei street [5, 93].

Figure 5 is presenting some SEM images and an EDX analysis. The micro structural detail in Figure 5b reveals the morphology of a quartz particle having small particles adsorbed on its surface. Small particles, having diameter in 1-10 µm, are positioned inside the valleys and on the particle surface. They can be included in PM10, PM2.5, and PM1 classes. These small particles belong to the clay, fact sustained by the elemental composition in Table1, which is in good agreement with XRD observations, Figure 5c.

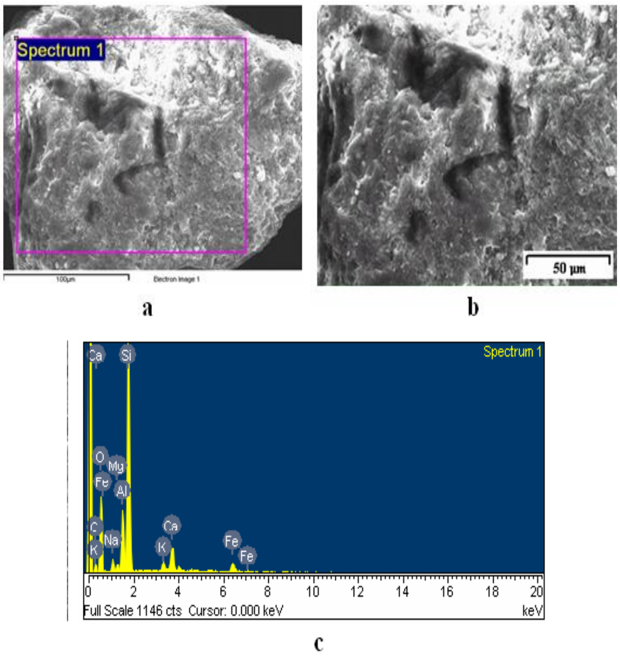


Fig. 5. SEM images of dust sample from Dâmboviţei street:
a) average magnification, b) high magnification, and c) EDX analysis of quartz particles [5].

Table 1) Elemental composition of Dâmboviţei street dust [5].

Element	C	O	Na	Mg	Al	Si	K	Ca	Fe	Total
Weight, %	17.75	49.95	2.61	0.75	5.45	19.43	0.65	2.13	1.28	100
Atomic, %	25.79	54.48	1.98	0.54	3.52	12.07	0.29	0.93	0.40	100

AFM images resulted for the small particles adsorbed in thin film are presented in Figure 6. Surface topography reveal two kind of particles, bigger ones having a height of about 28 nm and smaller ones having a height of about 13 nm. The same hierarchic structure is observed for the dust samples collected in autumn of 2010.

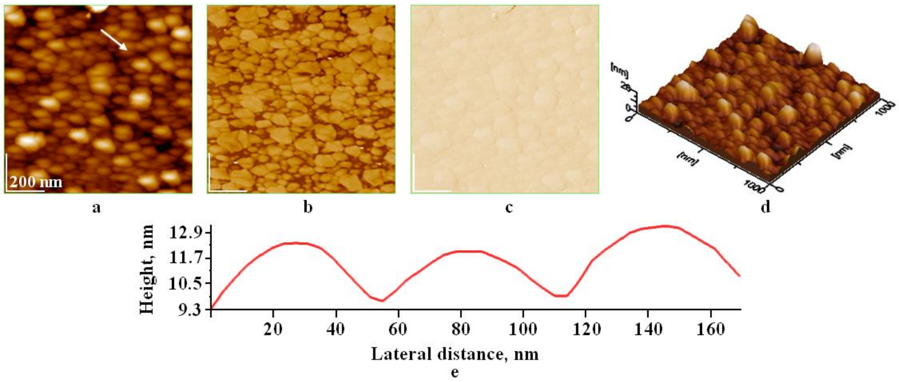


Fig. 6. AFM images of dust sample collected from Dâmboviţei street, adsorbed on glass: a) topographical image, b) phase image, c) amplitude image, d) 3D image of figure (a) and e) cross profile along the white arrow in figure (a). Scanned area: 1 µm x 1 µm [5, 93].

The particles adsorbed layer is compact with a high degree of uniformity, fact sustained by phase image in Figure 6b, where particles limit appears dark brown. Amplitude image, Figure 6c, shows that the scanning process occurs in the best condition without artifacts. The height distribution in the film structure could be observed better in 3D view of topographic image, Figure 6d. The average diameter of quartz particles is situated around 90 nm meanwhile clay particles feature a diameter of 40 nm as is observed in profile in Figure 6e. The measured values are in good agreement with the observations done on TEM images in Figure 7.

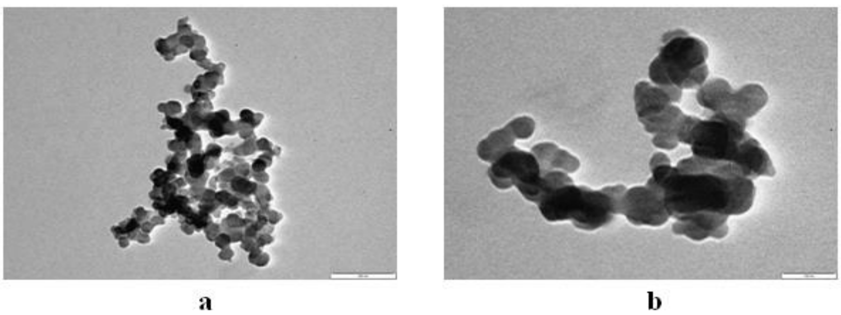


Fig. 7. TEM images of Dâmboviţei street dust in aqueous dispersion:
a) average and b) high magnification [5].

Some bigger particles having a diameter around 90 nm are observed in TEM images corresponding to the high particles observed at AFM investigation. These particles are darkening in TEM image due to their compact structure and rounded shape. The clay particles have a diameter around 40 nm similar to those observed by AFM, and exhibit a light gray nuance because of their translucence to the electron beam.

Dust from Aurel Vlaicu Street. Aurel Vlaicu street has a very intensive traffic, (25 cars/min.) and is the main access East route of Cluj-Napoca. An automatic station monitoring the quality of air (ARPM custody) was located on this street. The identified minerals from Aurel Vlaicu street sample can be observed in Figure 8.

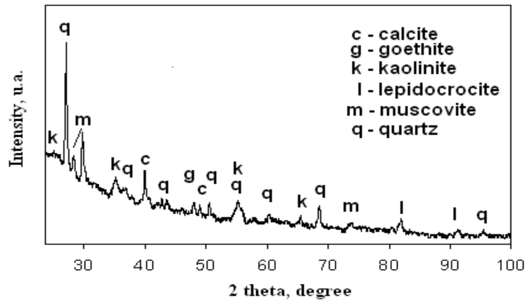
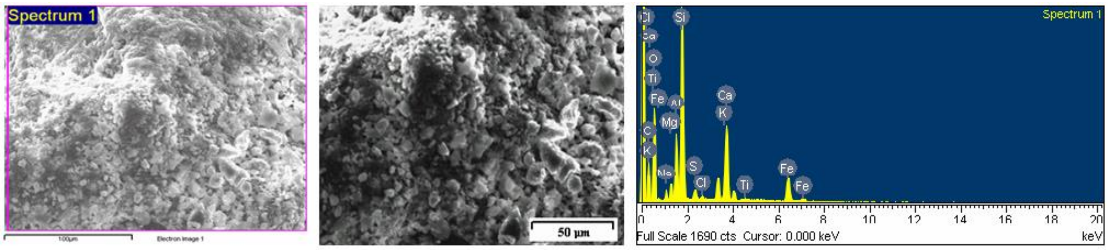


Fig. 8. XRD spectra of Aurel Vlaicu street dust [5, 91].

The dominant mineral is quartz showing very developed peaks throughout the sample followed by a mixture of muscovite and kaolinite. Calcium carbonate is found also, crystallized as calcite form. All these minerals are from natural sources (e.g. decomposition or erosion of soil). It was found trace of lepidocrocite and goethite crystallized as iron hydroxides [91, 92].

Microscopic fine particles from dust are shown in Figure 9. Fine fractions were visualized with SEM imaging and their elemental analysis was performed, SEM-EDX.



a b c

Fig. 9. SEM analysis for agglomeration of microscopic fine particles:
a) and b) SEM images, and c) EDX spectrum [5].

It was observed fine quartz particles mixture having from 5 μm to 25 μm diameters and include most of them in PM10 category. They are surrounded by fine particles with clays typical aspect, fact sustained by elemental composition, Figure 9c and Table 2. Their size range is from 2.5 μm and below included in PM2.5 and PM1 class risk. Elemental analysis evidences a typical composition for mixture of silicate particles, quartz and clay. Figure 9b shows the way of assembly of the dust in the street.

The aqueous dispersion of a representative sample, containing dust from Aurel Vlaicu street, allows the realization of an adsorbed layer on glass for AFM visualization, Figure 10, and an adsorbed layer on TEM grids for TEM investigation.

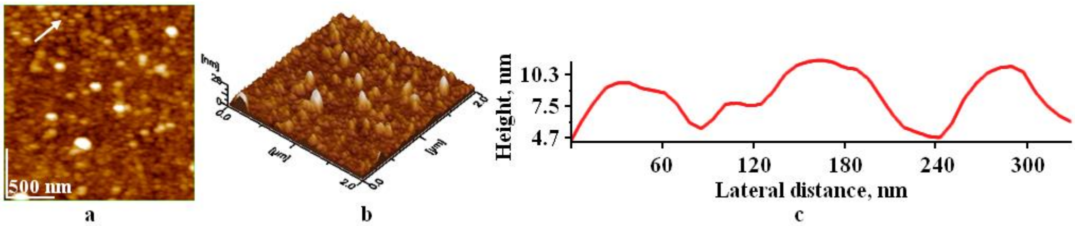


Fig. 10. AFM images of Aurel Vlaicu street dust sample, adsorbed on glass plate, optically polished: a) topographical image, b) 3D image of figure (a), and c) cross section along the white arrow in image (a). Scanned area: 2 µm x 2 µm [5, 91].

The topography, Figure 10a, shows a hierarchical deposited film with some rather big particles which present an average diameter of about 90 nm and the maxim height of the scanned area is about 28 nm, as shown in Figure 10b. They are surrounded by fine particles of about 10 nm height having the diameter between 40 and 60 nm as seen in cross section, Figure 10c.

4. Organization of micro- and nano-particles from atmospheric suspensions

4.1. Floating particles (FP) collected from atmosphere

Particulate matter from the air (PSA) is an important object of environmental protection study being a direct correlation with the sources they have produced. In Cluj-Napoca, the powdery emissions in the atmosphere are continuously monitored using a network of monitoring air parameters automatic stations of Regional Agency of Environmental Protection, Cluj-Napoca.

The quartz mineral is dominant in PSA Dâmboviţei sample followed by the clay minerals (muscovite and kaolinite); calcite and feroxide minerals (goethite and lepidocrocite), Figure 11. Mineralogical composition is similar to the dust from Dâmboviţei street, fact that proves the origin of PSA in street dust. Particulate matter sample collected from air using the automatic station from Aurel Vlaicu street was investigated with X-ray diffraction. It results a similar composition with the dust situated in the proximity of air monitoring station.

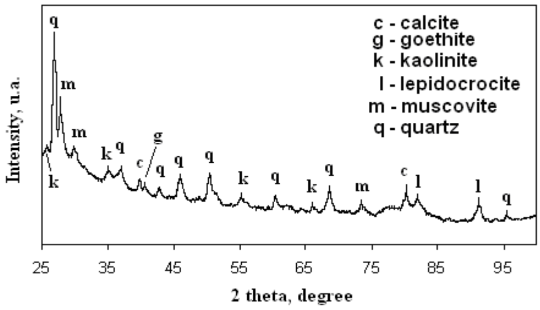


Fig. 11. X-ray pattern for particulate matter sample collected from the air, Dâmboviţei street [5, 93].

These minerals have been identified: quart, clays (muscovite and kaolinite), calcite, lepidocrocite, and goethite. The mineralogical composition is strong evidence that the buoyancy particles in the air have their origins in street dust.

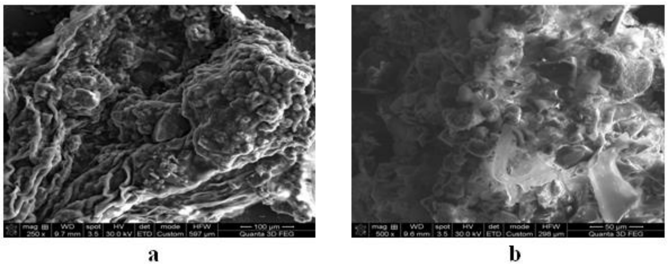


Fig. 12. SEM images of PSA evidenced in the powder material collected from air: a) Dâmboviţei street and b) Aurel Vlaicu street [5].

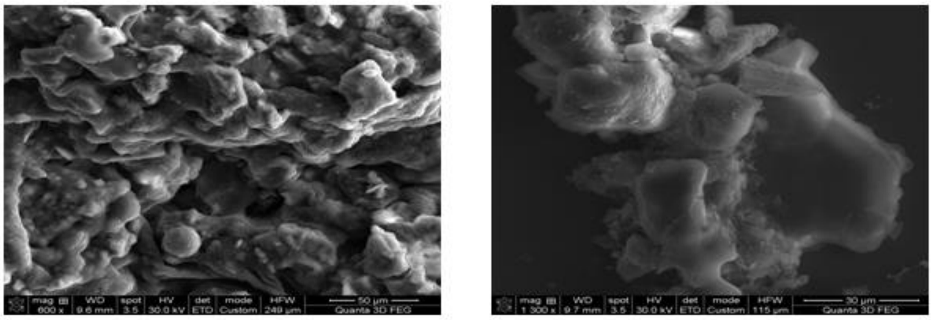
The morphological and dimensional aspects highlighted by the optical microscopy techniques are sustained and confirmed by SEM imaging, the images corresponding to the two representative sample of particulate matter from air is shown in Figures 12a and b. The information given by SEM analysis is made of similar results like the one of EDX summarized in Table 1 for Dâmboviţei street and Table 2 for Aurel Vlaicu street.

Table 2) Elemental composition for agglomeration of fine particles from Aurel Vlaicu street [5].

Element	C	O	Mg	Al	Si	S	K	Ca	Ti	Fe	Total
Weight, %	19.14	53.48	1.10	4.60	13.31	0.33	1.01	4.36	0.21	2.44	100
Atomic, %	27.39	57.44	0.78	2.93	8.15	0.18	0.44	1.87	0.08	0.75	100

4.2. PM10 from different locations

PM10 morphological aspects are similar for the both samples in SEM images, Figure 13. The samples characteristics show rounded-angular quartz particles in a dimensional range which belongs to the PM10 category. These particles are surrounded by fine particles, which vary from 1 to 2.5 μm, included the PM1 and PM2.5 fractions, in the visual field of the images.



a b

Fig. 13. SEM images of PM10 evidenced in particulate material collected from air: a) Dâmboviţei and b) Aurel Vlaicu streets [5].

The most of fine particles characteristics present tabular-lamellar shape typical for the clays category. Quartz particles are significant smaller than those observed in street dust sample and the clay particles are finest showing a strong tendency to cohesion. Clay particles are sensitive to environmental factors due to their high cleavages ability under the influence of mechanical stress [84]. The binding effect of micro dimensional clay, in the presence of humidity, has large industrial applications such as metal casting and alloys which was highlighted in other studies [85]. Such a binding effect is observed in Figure 13b, for the clay components in FP which presents a big cohesion among quartz particles.

The highlighted particles from PM10 samples are sensitive to physical and chemical factors of environment (e.g. wind, rainfall). Urban environment around Dâmboviţei and Aurel Vlaicu streets allow medium intensity of air currents formed by heavy traffic in sunny days and slight increase in days of storm. The PM10 emission chart for April 2013 is presented in Figure 14.

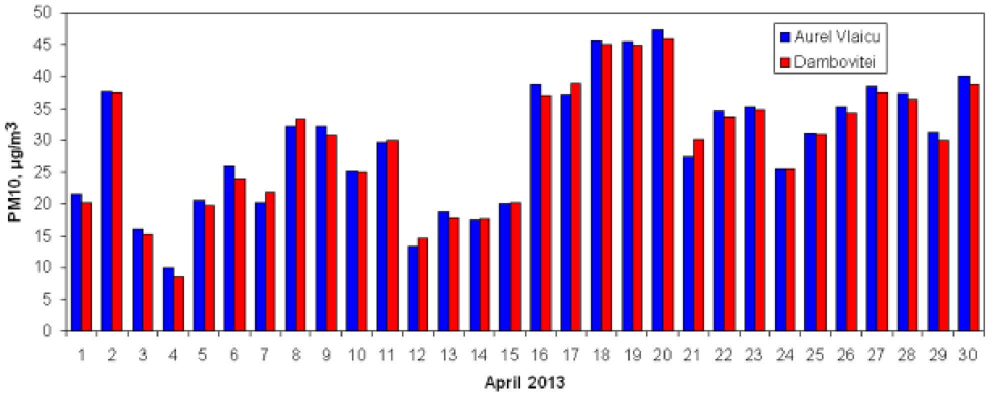
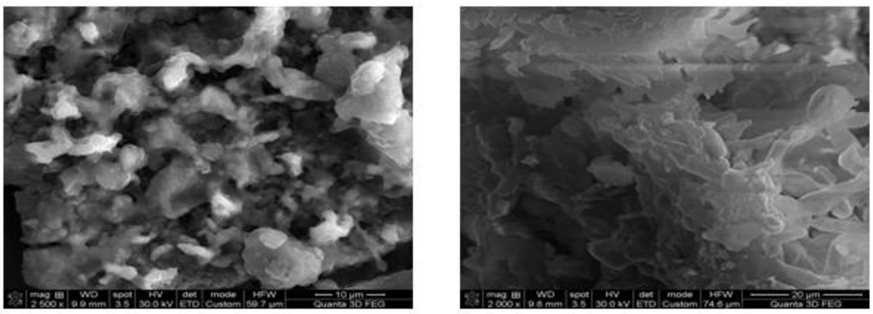


Fig. 14. PM10 emissions level measured with monitoring stations of air quality from Dâmboviţei and Aurel Vlaicu streets [5, 91] during April 2013.

Constant storms and air currents increase most of time the quantities of PM induced in the atmosphere [86]. Storms in Romania are usually related to significant precipitation depending on the continental temperature leading to natural purifications of PM in the atmosphere. Street dust conversion to particulate matters entrained in the air is explained by interactions of automobile traffic and adjacent environment which is in good agreement with the models presented in the literature [20].

4.3. PM2.5 from different locations

It was identified a lot of particles from PM2.5 class in particulate matter samples collected from air. These are ultrafine particles of clay mineral and may contain traces of iron hydroxides. The morphologies of PM2.5 fraction for collected samples with monitoring stations of air from Dâmboviţei and Aurel Vlaicu streets, are given in Figure 15.



a b

Fig. 15. SEM images of PM2.5 in powder material collected from air: a) Dâmboviţei [5, 92] and b) Aurel Vlaicu streets [5].

The graph, Figure 16, presents measurement results for PM2.5. Very similar values were noticed of daily measured results of the two air monitoring stations. Accordingly both streets are affected by the same mechanisms as possible pollutant from a common street dust susceptible to be in the atmosphere.

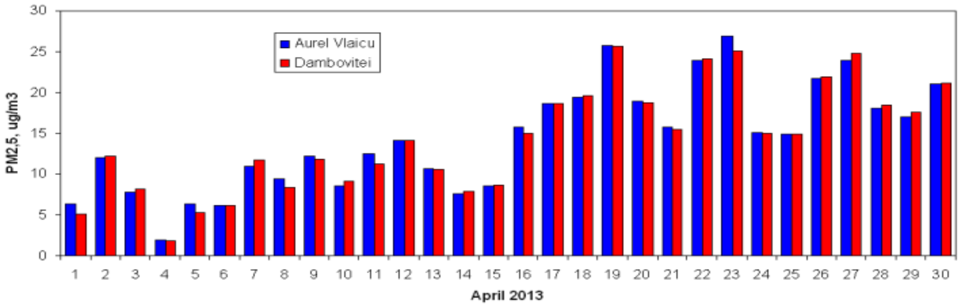


Fig. 16. PM2.5 emissions level measured with monitoring stations of air quality from Dâmboviţei and Aurel Vlaicu [5, 91] streets during April 2013.

4.4. PM1 from different locations

Recent investigation in the field of minerals found both natural and anthropogenic emissions from PM1 class [88, 89]. The tendency for PM1 emissions classification is obvious, particularly because there is no clear evidence of sub-micron fractions observed in the open atmosphere [90]. Such fine particles emissions are credited with combustion process (e.g. soot and acids aerosols).

AFM imaging helps visualization and analysis of particulate matters from PM1 class by scanning an area of such particles well spread on a solid support (e.g. glass) as given in Figure 17. The surface topography highlighted rounded particles (typical aspects for quartz) having diameter up to 1µm, and being surrounded by fine particles.

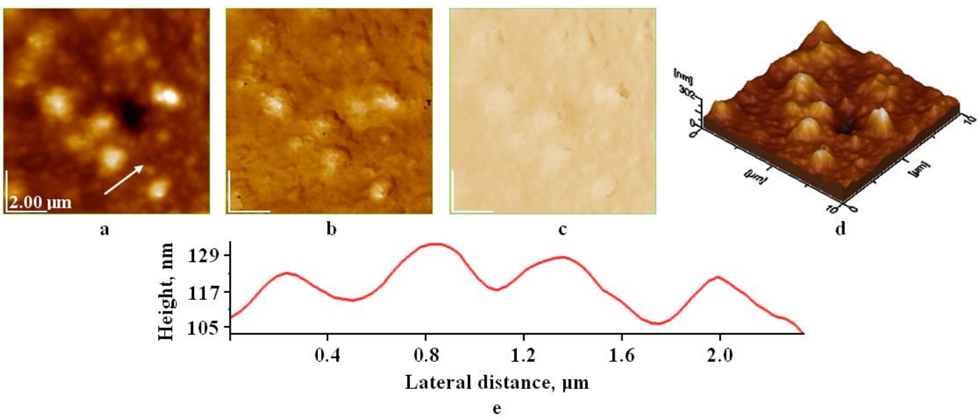


Fig. 17. AFM images for PM1 sample from Dâmboviţei street, adsorbed on glass. Symbols as in Fig. 6. Scanned area: 10 µm x 10 µm [5].

The adsorbed film is rather compact as observed in the phase image, figure 17b and in amplitude image in Figure 17c. PM1 particles (high height ones) are arranged on a sub micrometer fraction (low height). This situation is similar to that observed in TEM images, where nano-particles were also noticed. The profile in Figure 17e shows these fine particles, with an average diameter of 300 nm. Considering the multitude of particles that appear in the street dust and in atmospheric suspensions in Dâmboviţei and Aurel Vlaicu streets, it is rational to propose the emergence of a new class of particulate matter in the air that could be called PM0.5.

4.5. Discovery of PM0.5 fraction as a new found component

Aqueous dispersions of particulate matters collected from the well stirred air and adsorbed on glass plates were used to evidence the constituent particles. The adsorbed layers were used for X-ray diffractions (XRD) and for AFM imaging.

Two things were followed by XRD analysis, namely the establishing of minerals nano-particles nature in the deposited film, Figure 18, and the determination of the average diameter using Scherer's relation, Table 3. Thus, it has registered some spectra at small angle to catch peaks well developed especially for clay minerals. A low speed mode (0.5 two theta degree/minute) was used to ensure the optimum development of diffraction peaks.

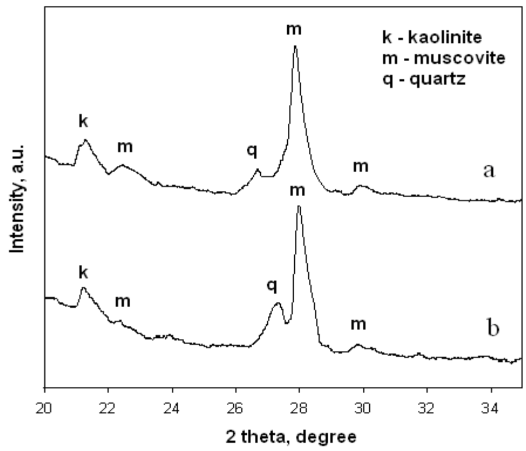


Fig. 18. XRD spectra for fine fraction particles collected from air: a) Dâmboviţei street and b) Aurel Vlaicu street [5].

Table 3) Nano-particles diameter resulting from XRD spectra [5].

Mineral	Particle diameter, nm		
	Dâmboviţei	Aurel Vlaicu	Rounded
Kaolinite	40.12	58.49	60
Muscovite	59.24	58.99	60
Quartz	90.12	92.37	90

The adsorbed film of nano-particles, collected from the air in Dâmboviţei street, is visualized in Figure 19a. Topographic image reveals two ranges of particles having around 90 nm, in good agreement with the quartz nano-particles size, and particles with typical morphology for clay, having diameters between 40 and 60 nm.

The amplitude image, Figure 19b, shows clearly the particular contour of each nano-particle arranged within the adsorbed film. Its morphology is illustrated in 3D image, Figure 19c, where in addition to particles with diameter 40-60 nm, some ultrafine particles are observed surrounding the larger ones. Their average diameter is about 20 nm (Figure 19d), indicating a progress of clay material fragmentation in the atmosphere, with dangerous potential for humans due to their very small size.

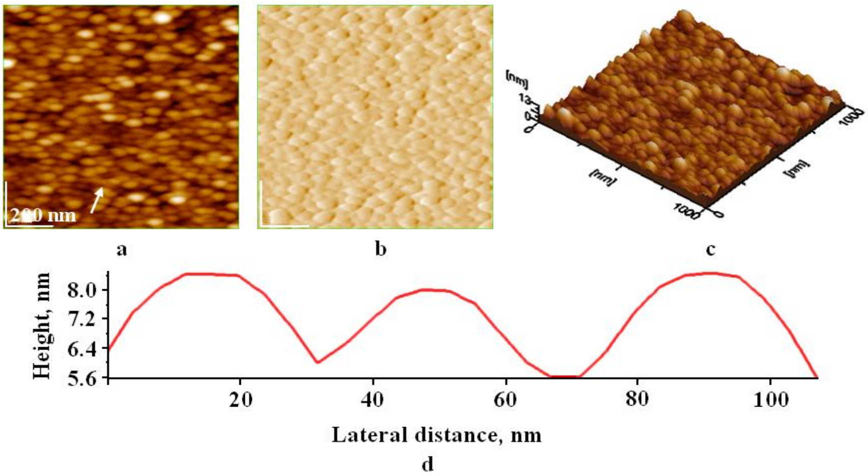


Fig. 19. AFM images for submicron particles from Dâmboviţei street; a) topographic image, b) amplitude image, c) 3D image of figure (a), and d) cross profile along the white arrow in the image (a). Scanned area: 1000 nm x 1000 nm [5].

A similar correlation was observed for nano-particles (Figure 20), collected from the atmosphere in the Aurel Vlaicu street. Their features are in good agreement with crystallographic model of clay. More particles with larger diameter situated around of 90 nm, were identified, they are mostly quartz particles. The edges of the mineral particles are highlighted with high resolution in phase image, Figure 20b.

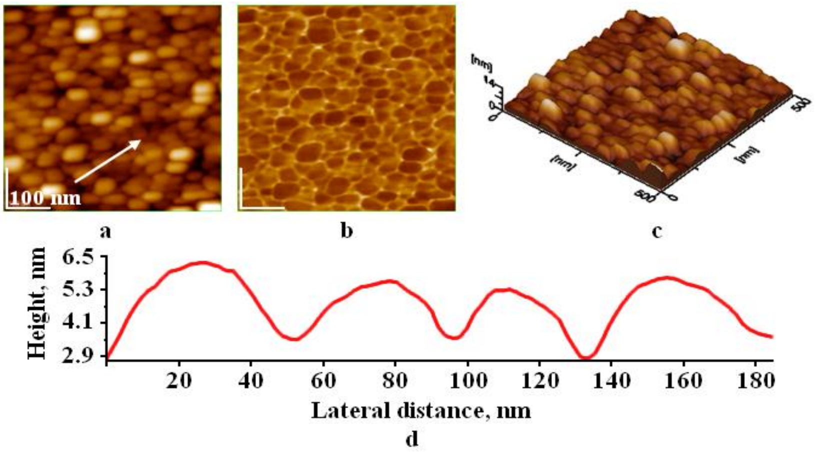


Fig. 20. AFM images for submicron particles from Aurel Vlaicu street; a) topographic image, b) phase image, c) 3D image of figure (a), and d) cross profile along the white arrow in the image (a). Scanned area: 500 nm x 500 nm [5, 91].

The height of adsorbed layer is given in a 3D topography, Figure 20c. The cross profile, Figure 20d, shows a mean diameter ranging from 40 to 60 nm, in good agreement with the results obtained by Scherer's formula from XRD patterns.

5. Potential measures for particulate matters pollution diminishing

The second objective of this investigation is to figure out possible strategies for air quality management, AQM, improvement based on the physical and chemical data obtained from the investigation of samples collected from these areas of interest.

Urban air quality management, UAQM, requires specific practices in each distinct city region [94, 95]. They have the testing, evaluation, and measurement of environmental pollutants in order to maintain the air quality as clean and acceptable for human health as priorities.

Thus, to materialize such a management, the European Union adopted and implemented environmental legislation such as Directive 1999/30/CE [96] and Directive 2008/50/CE [29] stating targets and maximum permitted values for particulate matter. The directives objective consists in adequate information of air quality and ensuring that this information was made available to the public by notice boards or on the website of the Protection Environmental Agency [97]. This leads to awareness and responsibility, prevention, and repair of environmental damage for those who bring negative impact to nature and health.

An adequate management has suitable measures in case of exceeding the maximum permitted values for particulate matter due to multiple sources that produce them. These measures are intended to reducing PM10, and PM 2.5

concentrations by increasing green areas and their maintenance, continuous improvement of sanitations services in the city, providing a more environmentally friendly transportation, encouraging the use of public transportation and even the use of bicycles, rehabilitation and modernization of city infrastructure and public awareness about the importance of such measures to reduce air pollution [97]. Greater cities have great problems with air pollution with particulate matters, case of Mumbai (Bombay) India with a population over 9.9 million people and a clogged traffic infrastructure combined with strong industrial facilities [98]. Their main strategy for environment management was severe monitoring of pollution issue by implementing of international air pollution regulation. Car traffic and industrial facilities were controlled by the authorities in a strictly manner to respect the international regulation.

Comparing to India, Romania has already implemented the international air regulation [29, 96]. They are applied and verified by the Environmental Protection Agency. Fortunately, this agency in Cluj-Napoca has a network of Automatic Stations, AS, for air quality monitoring including PM classes. Samples collected from atmosphere with those stations were subjected to physical and chemical investigation in order to obtain reference values for improvement of the management strategy. The experimental results were focused to a major discovery of the submicron fraction PM0.5. Data were published in several articles [81, 82, 91-93], and in a PhD dissertation [5].

Moreover, in this review the mechanism of formation, release and lifting into the atmosphere of various particulate matters (powders) is revealed. Certainly, the relationship between street dust and multiple sources as well as the lifting process of particles in the air and the interaction among them are important for the formation and propagation of particulate matters in the atmosphere. In the case of consistent dust still monitoring the sources, the street dust can be collected with the street vacuum cleaner resulting in less dust and likely particulate matter to entre in the atmosphere. Thus, the street dust needs to be collected, processed, stored, and well neutralized. A good environmental management will consider the environmental care in the streets proximity, so the formed dust is in small amounts and can be collected and stored.

The street dust in the air due to building construction and demolition activities can be avoided by wet deposition method in special waste dumps [99, 100]. Such strategy moves the pollution from the city to the dump place. If the dust is not enough wetted it will be re-suspended in the atmosphere. If the dump is not well consolidated the meteorological water could wash the dust particles conducting to water pollution [101]. Therefore, a strategy for dust particles converting to fertile soil is required. Some physical and chemical facts concerning these fine dust particles prove to be helpful as follows.

5.1. Nano-particles bonded into larger fractions

Generally, smaller particles are attracted by larger ones in accordance with universal gravitation law, fact more pronounced when the particles exerting attraction are 10 or even 100 times larger than the attracted particles.

The layer adsorbed, from aqueous dispersion of dust fine powders collected in Dâmboviţei street, on glass contains some sub-micron particles surrounded by nano-particles, Figure 21. The topography Figure 21a shows sub-micron particles with an average diameter around 250 nm, highlighting a strong attraction among them aligned in rows. Phase image, Figure 21b, amplitude image, Figure 21c, and 3D-topography, Figure 21d show an advanced compactness of adsorbed film. Sub-micron particles have a local height of about 84 nm while the nano-particles are situated at an average height of about 30 nm (Figure 21d). Average diameter of nano-particles is around 40 nm as observed in the cross profile, Figure 21e.

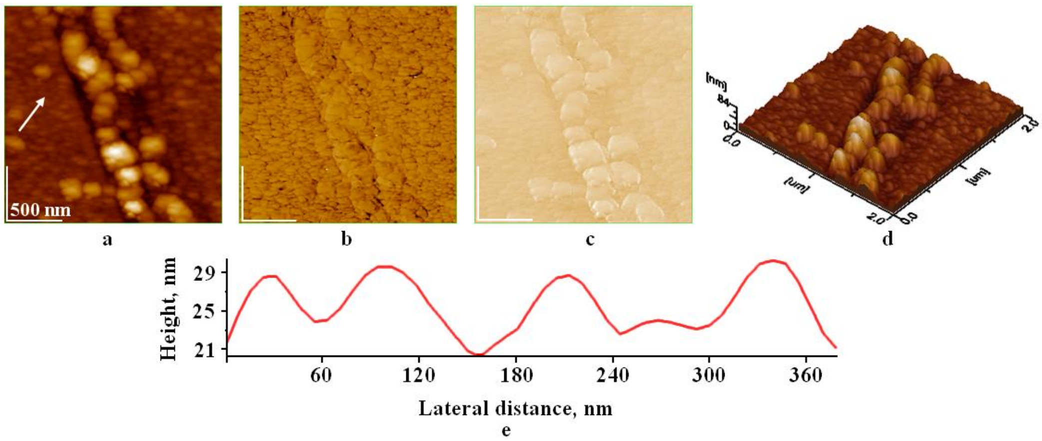


Fig. 21. AFM images for sub-micron particles (clusters) surrounded by nano-particles adsorbed on glass surface. Symbols as in Fig. 6. Scanned area: 2 μm x 2 μm [5].

Thus, Figure 21 exemplifies how the particles about 250 nm in diameter bind on their surface particles of 40 nm in diameter. Once this structural cluster is formed, it increases continuously by the uptake of new nano-particles, if meets favorable conditions. This phenomenon is similar with the heterogeneous crystallization where the nano-particle plays the role of seed. It was observed that the moisture environment facilitates attraction and nano-particles bind on sub-micron particles.

5.2. Ultrafine particles coalescence

The particles coalescence depends on their mobility. It is very low in solid phase but dispersed into gaseous phase it increases very fast. The experience reveals that a proper coalescence between ultrafine particles is favored by wet environment.

The dosage of appropriate amount of water is the success key for the small particles cluster formation. This way could be useful to produce macroscopic aggregates of micro and nano-particles to assure a better handling. The reintegration into the fertile soil is preferred. Such soils could be used for the reconstruction of decayed green areas in the parks and streets adjacent areas.

5.3. Street dust agglomeration and binding into stabile soils and their recycling

As observed from the analyzed data in current review, dust particles lead to hazardous pollution scenario which affects living neighborhood as well as recreational areas. European quality of life survey reveals the importance of diminishing the dust sources [102, 103], especially due to the health risks [39-41,104].

The simplest method for street dust conversion to environmental soil is the assimilation of controlled dose of street dust in a fertile soil. The street dust must be raw sieved to remove the trash and big particles, then watered to form pellets, which are mixed together with affined soil, in a mixing reactor. Finally, it results soil for green areas rehabilitation. This strategy was implemented at laboratory scale. Some soil treatments were performed on controlled environment, using blended soils, like a mixture of 25% street dust with 75% fertile soil. This mixture was tested using dahlia bulbs. The dahlias rise up from the treated ground, and this mixture allows a proper plant growth.

Conclusions

The experimental tests were achieved by measuring the particles composition, size and shape as well as their structure and morphology in the street dust and the atmosphere in various regions of Cluj-Napoca, Transylvania, Romania, by using the suitable chemical methods and top physical techniques, like XRD, AFM, TEM and SEM-EDX. The experimental results showed that particulate matters, PM10, PM2.5, PM1 and PM0.5, as well as nano-particles were found depending on the various sources of particles, city regions, seasonal meteorology and diurnal activities. Accordingly, the developed strategy for the improvement of air quality management is based on the evaluation of urban pollution and is efficient for the maintenance of a reasonably clean air in Cluj-Napoca city.

The risks associated with PM10 and PM2.5 particulate matters were identified in the state of the art and their maximum admissible values have been associated with air quality index. The PM1 and PM0.5 fractions as well as nano-particles and their maximum admissible limits will be standardized in the near future.

The discovery of PM1 particles in the street dust is one of the most important achievements of this investigation. This category includes fine particles with the diameter up to 1 μm. The performed analysis on various samples of street dust and particles collected from atmosphere revealed nano-particles of clay having 40 up to 60 nm diameter and quartz particles having an average diameter of about 90 nm. The submicron particles, such as PM0.5, were also identified, and are probably formed by coalescence and self-association of ultrafine particles or by the fragmentation of larger particles. The identification of nano-particles in the street dust is a scientific premiere.

Acknowledgment

The author, Gertrud-Alexandra Păltinean, acknowledges the financial support from UEFISCDI trough the grant no. 241.

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