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# PARTICULATE MATTERS FOUND IN URBAN STREET DUST

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**ABSTRACT.** This investigation was carried out to characterize the composition of different particulate matters (PM) in urban street dust. Samples of street dust were collected on a weekly basis for three summer months from the intersection of Bucharest Avenue and Paris Street in Cluj-Napoca city, Romania. The samples were processed to determine the composition by X-ray diffraction. A large amount of minerals, such as quartz, kaolinite and calcite, and some traces of portlandite and goethite were found. Particle shape was investigated by optical transmitted light and cross polarized light microscopy. The data revealed a wide range of particle size, from a few μm to several hundred μm. The surface morphology and the size distribution of different submicron particles were confirmed by AFM on various thin films of particulate matters deposited on glass support from aqueous dispersion drops, taken out at different sedimentation times. The fine particles observed by AFM had the diameter between 100 and 180 nm and they correspond to kaolinite. Chemical characteristics of urban street dust indicate that the particulate matters have a natural and an anthropogenic origin. Particulate matters, such as $PM_{2.5}$ and $PM_{10}$, as well as the fine kaolinite particles found in the urban street dust are very dangerous for lung health due to the potential risk of silicosis.

***Keywords:*** *street dust, particulate matter, particle size, morphology, chemical composition, X-ray diffraction, AFM*

## INTRODUCTION

In urban areas, the pollution becomes one of the common ecological problems at world scale and particularly at Cluj-Napoca city, in Romania. For instance, street dust particles deposited on roads originate from the interaction of liquid, solid and gaseous materials produced from various sources. Chemical components and their quantity in street dust are considered indicators of the environmental pollution.

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Fine microscopic particles (PM) from street dust have been shown to increase the risk of silicosis [1, 2]. These studies found that the most affected subjects are pedestrians and people working in the street. The potential risk is considerably increased by fine particles, like $PM_{2.5}$, mainly when they were burned in a combustion engine.

Usually, there are two main street dust sources, the natural one from the disaggregation of soil particles, such as kaolinitic beds erosion [3], and the anthropogenic source consisting primarily of the built space erosion, such as building facades erosion [4, 5].

The amount of dust from each source depends on the distinctiveness of the investigated area, like the degree of infrastructural development and the presence or the absence of green places in that region. On the other hand, the urban streets act like sinks for vehicle emissions caused by combustion of fuel. These emissions contain particulate matter (PM), which is released in the air and deposited on the road surface in the form of street dust.

The goal of the present investigation is to determine the chemical composition of urban street dust in Cluj-Napoca city of Romania. Samples were taken from the intersection of Bucharest Avenue and Paris Street. This area was selected because it is one of the areas in Cluj-Napoca with the most traffic and pedestrian flow, where an increased risk of PM exposure appears for humans and other living organisms. Dust samples were collected weekly during the summer time (see, Experimental Section), because summer is already recognized for high pollution in Cluj-Napoca.

## RESULTS AND DISCUSSION

The representative combined sample of the urban street dust is a complex material having several minerals in its composition. Generally, the best tool for mineral analysis and crystal phase identification is the X-ray diffraction [6, 7]. The obtained X-ray diffraction data for the representative combined dust sample is presented in Figure 1.

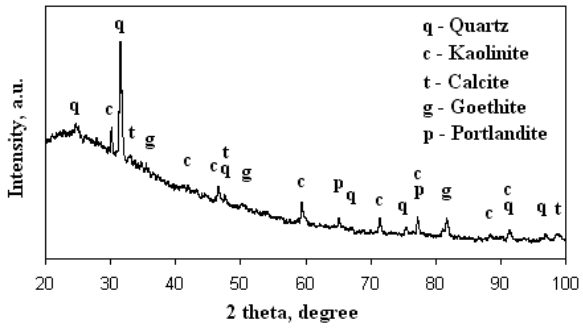



**Figure 1.** The X-ray diffraction data for the combined sample of urban street dust, collected from the intersection of Bucharest Avenue and Paris Street in Cluj-Napoca, during the summer time of 2009.

The analysis of X-ray diffraction patterns (Figure 1) shows large amounts of minerals, such as quartz, kaolinite and calcite, within the combined dust sample. Additionally, trace amounts of portlandite and goethite were also found.

The dominant mineral, indicated by the most intense peak, in Figure 1, is formed by quartz particles. The chemical formula of quartz is $SiO_2$, having a hexagonal crystal lattice and showing an irregular rounded aspect [8]. Because the hexagonal crystallization of quartz does not allow cleavage, the bigger quartz particles break and form very small and sharp fragments (slivers). Silica fragments are often found in nearby road soils and fallen plaster from eroded buildings.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is found in clay minerals [9]. It crystallizes in a monoclinic crystal system having a tabular aspect spread in a wide range of particle sizes from nanometric to large micro scale. It appears as a common component in gardening soils and also it could be found in construction materials. Thus, kaolinite is more likely found in street dust as a natural source due to the eroded soil.

Calcite ($CaCO_3$) is also known as limestone [10], and it is often found in soil. The calcite particles appear as a result of the disaggregation of lime stones during the marl formation. It is present in street dust via natural source.

Portlandite ($Ca(OH)_2$) is not a soil component but it appears often in building plaster [11]. Its presence in the street dust sample is likely due to building erosion.

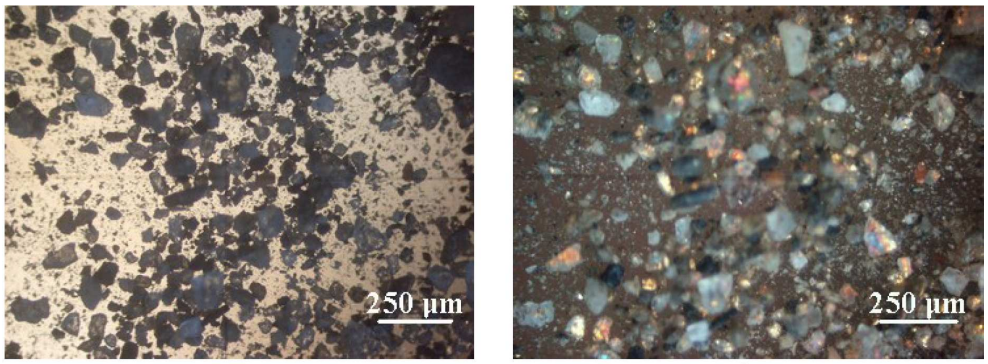
Goethite ($Fe_2O_3 * H_2O$) known as rust appears in trace amounts in the combined dust sample. Its presence could be explained by the corrosion of car chassis [12]. The presence of goethite is due to anthropogenic activities.

Taking into account, the low concentration of portlandite and goethite in the combined dust sample in comparison with large amounts of quartz, it is reasonable to assume that the anthropogenic dust source has a secondary contribution in the street dust formation.

Figure 2a presents optical microscopy investigation of combined dust sample featuring a wide range of particles having different shapes. The diameter of particles varies up to 200 μm.

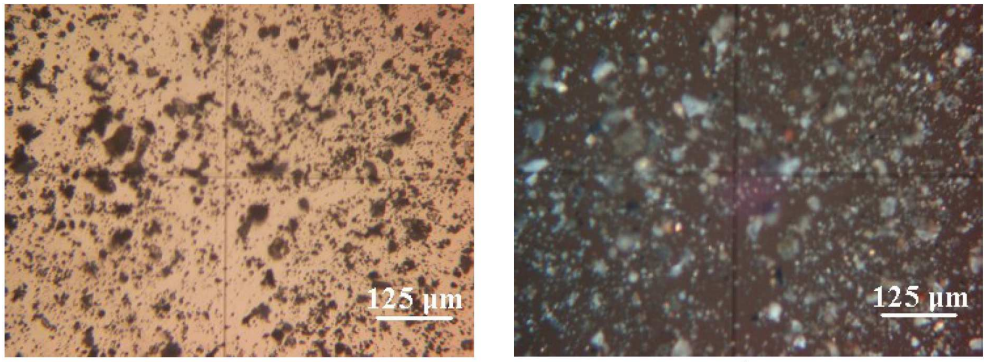
The shapes observed in Figure 2a vary form rounded shapes belonging to quartz to tabular one typical for kaolinite. In cross polarized light, Figure 2b, the particles appear in specific colors depending on their orientation and the position angle to the optical microscope axis. Quartz particles are colored in green-gray, kaolinite particles appear in yellow-red color, depending on the position angle, and calcite particles appear in a light yellow color [13].

Goethite usually appears in cross polarized light on a blue color, but in very thin slices it appears in blood red color. The results, shown in Figure 2, correlate substantially with the observation given in the X-ray spectrum, thus proving the goethite presence only as trace amounts.




a b

**Figure 2.** Optical light microphotographs of dry combined dust powder: a) in transmitted light; b) in cross polarized light.




a b

**Figure 3.** Optical light microphotographs of a fine fraction obtained by sieving the combined dust powder: a) in transmitted light; b) in cross polarized light.

To emphasize on the small particles from the street dust sample, the larger particles, for example those with a diameter bigger than 150 µm, were removed by sieving the initial combined dust sample through a stainless steel sieve with mesh size of 150 µm. The obtained fine dust powder was then spread as a thin layer on the glass support and it was further investigated by optical microscopy (Figure 3).

In Figure 3a, smaller particles than 150 µm in diameter are identified. Analyzing Figure 3, it seems that, the large particles have the predominant diameter between 30 and 75 µm, with specific quartzite morphology. Much smaller particles are also observed in the diameter range of 2.5 and 10 µm. In Figure 3b, the bulky particles are colored in green/ gray and are specifically identified as quartzite. The fine particles are painted in yellow and dark brown and represent kaolinite. Additionally, some trace amounts of calcite particles are identified as intense yellow colored ones.

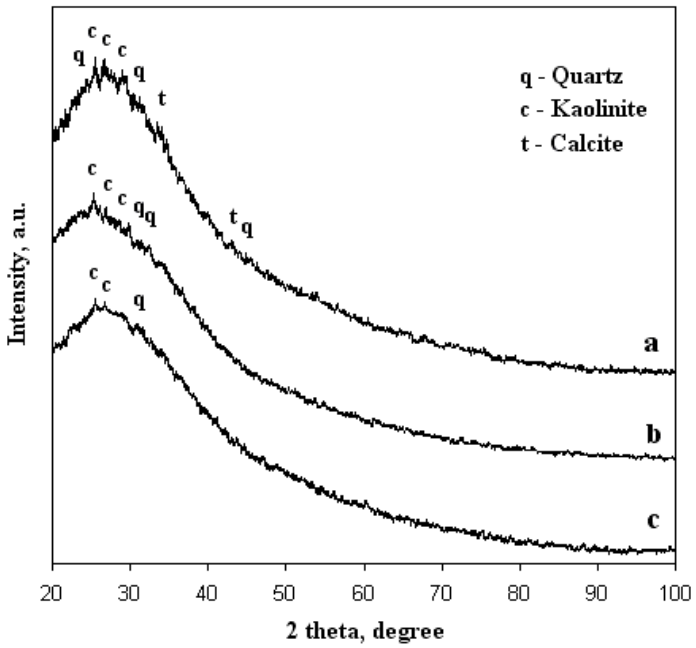



**Figure 4.** X – ray diffraction patterns of dry fine dust samples, taken out from dust aqueous dispersion, after several sedimentation times: a) 10 min; b) 15 min; c) 30 min.

The morphological and structural investigations of dust particles were further carried out on the fine dust obtained from the aqueous suspension of the combined dust in deionized water. For this purpose, the dilute aqueous suspension of dust was taken out at different times, namely after 10, 15 and 30 min, of sedimentation. The dried out fine dust powders obtained at different sedimentation times were used for X-ray diffractions (Figure 4) and microscopic measurements (Figures 5-7).

Structural observations (Figure 4, curve a) indicate that, for dry dust sample obtained at 10 min of sedimentation, the majority of dust parts are quartzite and kaolinite. The calcite is present in trace amounts. It is also observed that the intensity peaks are much smaller in comparison with the corresponding ones for the initial dry combined dust powder sample (given in Figure 1) and the curve shape is more bent due to the fine dust particles of micrometer size.

At 15 min of sedimentation, a complete disappearance of diffraction peaks of calcite is noted (Figure 4, curve b); the kaolinite is identified and quartzite is observed only in trace amounts. This indicates a rather quick sedimentation of calcite and quartz particles.

The X – ray diffraction patterns still remain even for dry dust, advanced processed at 30 min of sedimentation, but the quartz peaks almost disappear leaving only trace amounts of kaolinite (Figure 4, curve c).

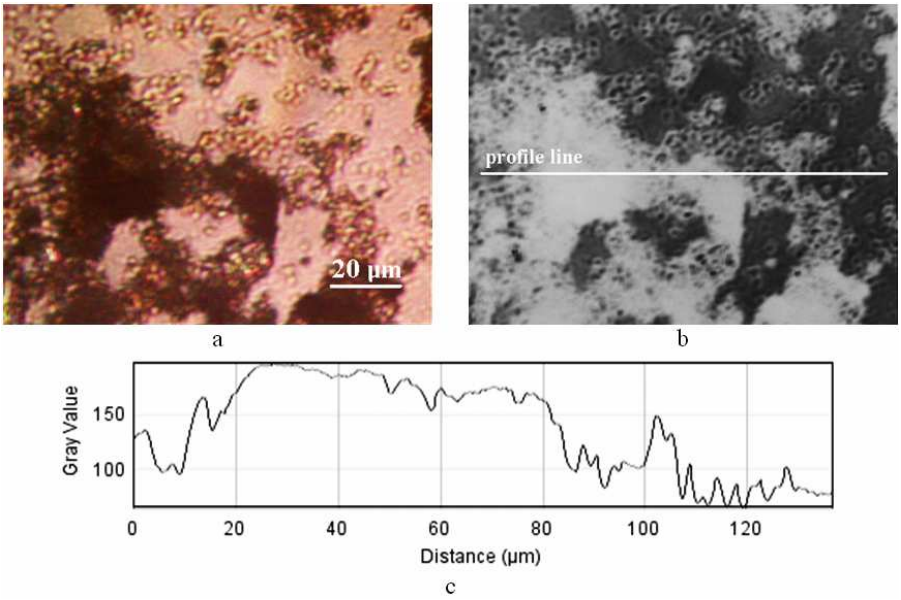



**Figure 5.** Optical microphotographs for the thin layer of dry fine dust, obtained after 10 min of sedimentation: a) transmitted light; b) negative gray scale representation of Figure 5a; c) profile detail on the corresponding line shown in Figure 5b.

To further explore the fine dust particles, the dust samples obtained at different sedimentation times, for 10, 15 respectively 30 min, were spread as thin films to be investigated by optic microscopy (Figures 5-7). A semi-quantitative analysis of these images was performed in order to establish an average diameter of dust particles.

In Figure 5a, two types of particles are observed, some larger particles with specific shape characteristic for quartzite and several smaller particles of kaolinitic specific form. This chemical structure is consistent with the data shown in Figure 4a.

Detailed profile (Figure 5c) shows an agglomeration of quartzite particles that is greater than 60 µm in diameter accompanied by a few fine kaolinite particles with diameter between 15 and 30 µm. The average particle diameter is about 50 µm.

The calcite particles disappear at 15 min as seen in Figure 6a, where there are some trace amounts of quartz particles with an average diameter of about 30 µm. The predominant particles are much smaller and show a specific kaolinitic habit. The profile in Figure 6c indicates an average diameter of kaolinitic particles of about 10 µm.

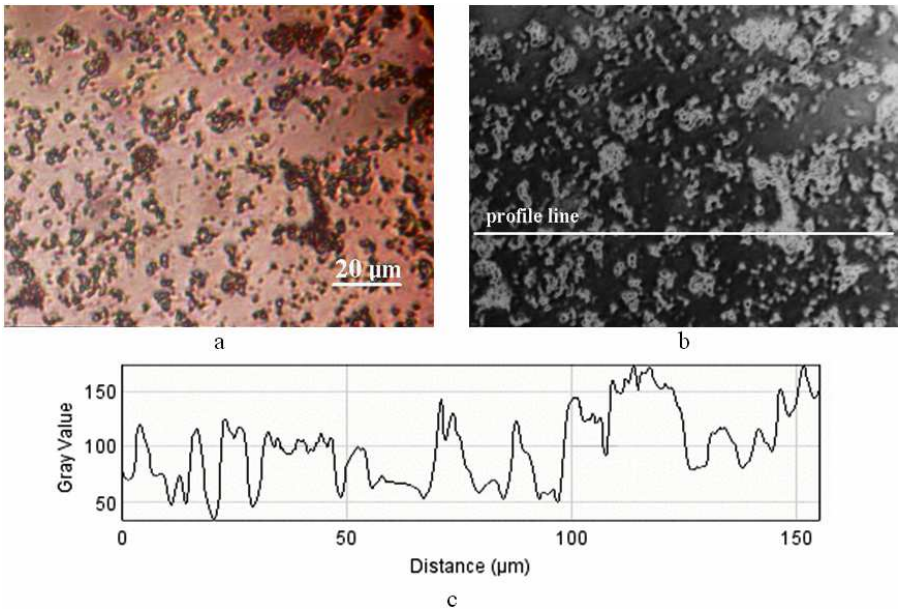



**Figure 6.** Optical microphotographs for the thin layer of dry fine dust, obtained after 15 min of sedimentation: a) transmitted light; b) negative gray scale representation of Figure 6a; c) profile detail on the corresponding line given in Figure 6b.

This major change (Figure 6) of particle size and shape distribution can be also seen Figure 4b, where a considerable decrease of the intensity of quartz peaks is identified. Thus, an assumption relative to a rapid sedimentation of quartz particles can be suggested. Kaolinite is a mineral with lamellar aspect susceptible to environmental factors and it can generate the very fine particles, tending to occupy an increasing space in the respective area of particles, in substantial agreement with Figure 6.

On the other hand, trace amounts of quartz show sharp corners, and they are actually broken down fragments from larger particles under the influence of environmental factors.

Details in Figure 6 are in good agreement with the information given in corresponding X-ray diffraction patterns (Figure 4b). The findings show that the kaolinite and trace amounts of quartz, in the sample obtained at 15 min of sedimentation time, can be treated as $PM_{10}$. Therefore, such particles show a fairly high risk factor for humans and other living beings.

Prolonged sedimentation (30 min) time of dust particles in aqueous suspension indicates that kaolinite and especially quartzite remain only as trace amounts in aqueous phase as shown in Figure 4c. In Figure 7a, the specific morphology of quartzite particles can not be identified. Only clay particles of kaolinite are identified showing varying size in agreement with data in Figure 4c.

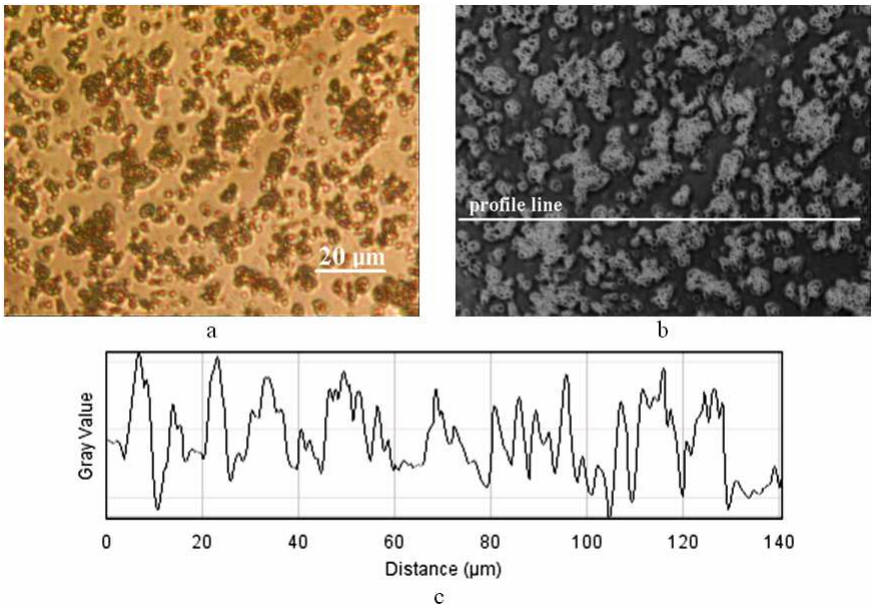



**Figure 7.** Optical microphotographs for the thin layer of dry fine dust, obtained at 30 min of sedimentation: a) transmitted light; b) negative gray scale representation of Figure 7a; c) profile detail on the corresponding line in Figure 7b.

Profile detail of Figure 7c shows an average particle diameter of kaolinite of about 5 µm. This size is closer to the critical value of $PM_{2.5}$, which increases the risk factor to humans.

Optical microscopy is not able to identify submicron particles for this purpose we need more profound investigation using AFM [14-16] on powders. Usually double adhesive tape allows a proper particle immobilization for AFM investigation. Dust particles deposited as thin layers on solid substrate, as glass support, confirmed to be an effective method, as also shown in optic microscopy.

For AFM investigation, a thin film of dry fine dust was deposited on glass slide, from suspension taken out at 60 min of sedimentation. The AFM images are presented in Figure 8.

The topography image, Figure 8a, present several submicron particles featuring the kaolinite aspect. On the phase image, Figure 8b, one distinct phase corresponding to kaolinite particles is observed on the glass surface. The borders of kaolinite particles are better observed in amplitude image, given in Figure 8c.

The maximum height of the thin layer of particles is shown in 3d representation of topography image (Figure 8d), and it is about 96 nm. The average diameter of particles is determined by the distance measured at the half height of the particle profile in the cross section (Figure 8e). The

average diameter of kaolinite submicron particles is determined of about 180 nm. Similar behavior of kaolinite particles was also reported by others using SEM images [17].

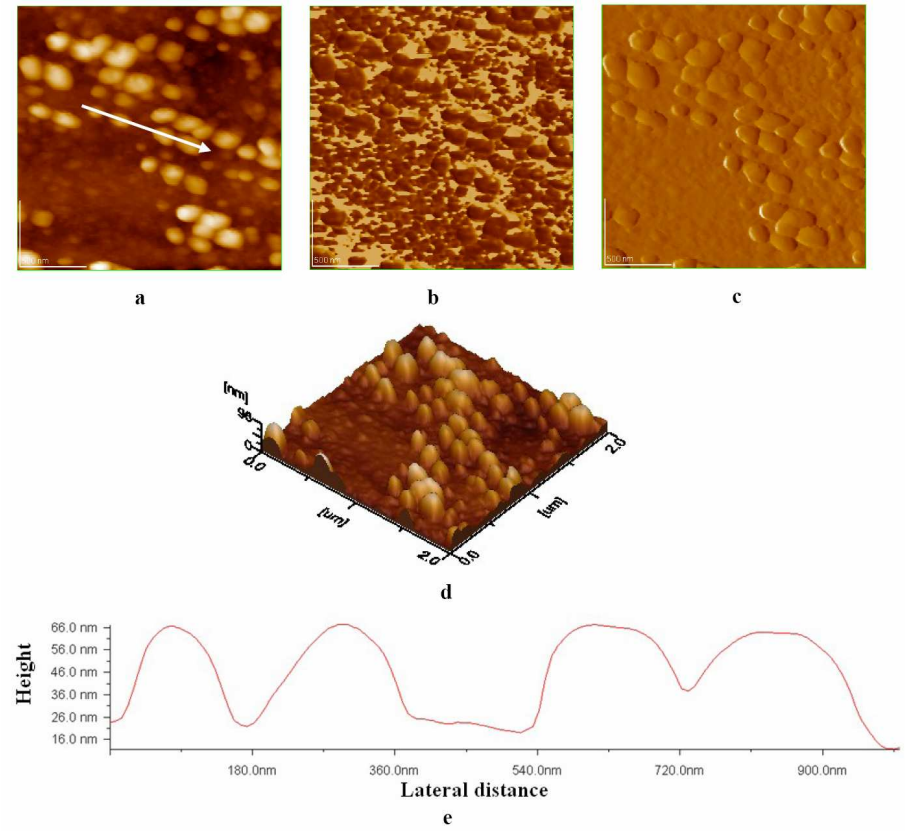



**Figure 8.** AFM images of the thin layer of dry fine dust, obtained at 60 min of sedimentation; a) topography; b)phase; c)amplitude; d) 3d view of image (a); e) cross section on the arrow given in image (a).

Some studies performed on fine and ultra fine particles of dust have demonstrated the implication of these particles in the shortness of breath [18, 19] which is strongly related to the cardio respiratory diseases and asthma.

## CONCLUSIONS

The investigated urban street dust was formed primarily by minerals from natural sources of dust, due to soil erosion and traffic conditions, as well as by some traces of particulate matter provided from anthropogenic sources.

The urban street dust was analyzed by X-ray diffraction and it contains rather large amounts of minerals, like quartzite, kaolinite and calcite as well as goethite and portlandite, as accompanying traces of main particulate minerals. Particle shape was investigated by optical transmitted light and cross polarized light microscopy both on native dust and on thin films of dust, obtained from aqueous dispersion at different sedimentation times.

The performed sedimentation analysis revealed that the larger particles were subjected to almost immediate sedimentation, while the fine ones remained in aqueous dispersion. The data revealed a wide range of particle size, from a few μm to several hundred μm. Thus, at 10 min sedimentation time, the average diameter of quartzite particles is greater than 60 μm and for kaolinite particles is between 15 and 30 μm. The estimated average diameter of particles is about 50 μm. After that, at 15 min of sedimentation time, the kaolinite particles are predominantly detected. Their average diameter is around 10 μm. Additionally, trace amounts of quartz was also found. Then, at 30 min of sedimentation, quartz almost disappeared and only kaolinite particles remained in aqueous dispersion. The average diameter of kaolinite particles is around 5 μm.

The surface morphology and the size distribution of submicron kaolinite particles were confirmed by AFM on thin films of dust adsorbed on glass support from aqueous dispersion at 60 min sedimentation time. The average diameter of fine kaolinite particles is about 180 nm. As stated above, because of the health risk of these fine particles we recommend a proper environmental management of the streets and adjacent places in the intersection of Bucharest Avenue and Paris Street in Cluj-Napoca city.

## EXPERIMENTAL SECTION

Street dust samples were collected once a week from the intersection of Bucharest Avenue and Paris Street in Cluj-Napoca, a residential and commercial area, over a period of three summer months (June 2009 - August 2009). For measurement consistency the dust samples were collected on the same day of the week using a conventional non metallic (e.g. plastic) broom and a plastic pan. This sampling procedure is similar to those reported recently [20]. Plastic containers were used to collect and store the dust samples. The samples were air dried. One average sample per month was prepared by mixing equal amounts (by mass) of dust samples from each week of the month, followed by thorough mixing. Then, a representative complex sample was obtained for the summer period by mixing equal amounts (by mass) of dust samples from each month (June, July and August of 2009), followed by thorough mixing. Portions of this representative combined sample of street dust were used for X-ray diffractions and optical microscopy observations.

Further, X-ray diffractions and optical microscopy investigations were carried on the thin films of representative dust sample, as follows. A combined sample of about 10 g of representative street dust was immersed in deionized water and consequently subjected to sedimentation. Aqueous dispersion drops were independently taken after 10, 15 and 30 min of sedimentation time and they were spread on glass plate and dried.

For AFM studies, the dust particles were immobilized from a dilute aqueous suspension, at 60 min sedimentation time, on a freshly cleaned flat glass surface, previously optically polished. A small amount of suspension, e.g. one or two drops, was taken out from a depth of 5 cm below the water surface and placed on the glass surface. The drops were spread on the solid support. The dust particles were dried at room temperature in a desiccator overnight. Particles with weak contact to the solid surface were removed in a dry nitrogen gas stream before AFM examination.

The X-ray diffraction analysis was performed on a DRON 3 diffractometer equipped with data acquisition module and the MATMEC VI.0 soft. A monochrome Co $k_{\alpha.}$ radiation was used for all X-ray spectra. The identification of minerals in the dust samples was carried out by comparing the obtained X-ray diffractions with the standard files of MATCH 1.0 X – ray standard data base from Crystal Impact Co.

Optical microscopy was performed on a Karl Zeiss Jena transmitted light microscope using transmitted light and cross polarized light method. Microphotographs were digital captured using a SAMSUNG 8 Mpx digital camera. The quantitative analysis of the optical microphotographs was performed by a professional soft Image J, as a free resource from National Institutes of Health, USA.

The AFM investigation was performed on a Jeol JSPM 4210 microscope in tapping operation mode using NSC 11 cantilever with resonant frequency of 330 kHz. The AFM topography, phase and amplitude images were acquired simultaneously at various scanned areas, as previously reported [21-26].

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