STUDIA UBB CHEMIA, LX, 2, Tom I, 2015 (p. 207-218)
(RECOMMENDED CITATION)

ENVIRONMENTAL IMPLICATIONS CONCERNING THE CHEMICAL COMPOSITION AND PARTICLE DISTRIBUTION OF ANTI – SKID MATERIAL

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ABSTRACT. Anti skid material (AM) used to improve the traffic conditions could affect the particulate matter emissions during winter. The investigated AM sample contains silica particles to improve the friction coefficient between tires and road surface and crystalline sodium chloride as anti glaze agent. We found also some interesting rusty particles containing iron hydroxide (lepidocrocite and goethite) mixed with fine quartz sliver. Compression test shows that those particles have a low strength being able to be disintegrated in harsh traffic conditions. The powder resulted after crushing of rusty particles feature fine fractions with diameter in the range of 1 – 10 μm. Such fractions were found in the collected sedimenting particles (SP) proving their ability to be suspended in atmosphere. The monitoring performed with Automatic Monitoring Air Quality Stations shows the average values for $PM_{2.5}$; PM_{10} and SP are below the maximum accepted limit. However the registered values were high in days with intensive car traffic and lower in other days. The situation could be improved by a proper sorting of rusty particles from re-circulated anti skid material.

Keywords: *anti - skid material, particulate matters, lepidocrocite,* PM_{10}, $PM_{2.5}$

INTRODUCTION

Particulate matter (PM) monitoring is one of the main environmental issues in the European Union. Several regulations were adopted in order to develop a suitable management of such emissions [1, 2]. PM_{10} and $PM_{2.5}$ are the reference for particulate emissions from various urban activities [3, 4]. The health risk is increased for the monitored particulate matter emissions (e.g. $PM_{2.5}$ and PM_{10}) due to their ability to be inhaled. The risk depends on the aerosol size and the breathing air velocity [5], related to the possibly

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harmful components. Previous studies show a heterogeneous composition for PM_{10} and $PM_{2.5}$ which contains mainly minerals but also organic phases depending on the source. Anthropogenic activities, as well as acid rain and particulate emission, present erosive action on the environment being a major source of particulate matter [6, 7]. Another major anthropogenic source is the automotive traffic by combustion emission as well as floating mineral particles suspension due to the air currents.

For instance, automotive traffic PM emission measured in 2011 in Istanbul shows 28.5 % in winter and only 3.9 % in summer [8]. Why more PM emission in winter? It is an interesting subject to follow. The automotive traffic particulate emission have two major sources: combustion particles such as soot and organic aerosols (which depends on the each car combustion system and filters) [9, 10] and mineral fine fractions resulted from the tires interaction with the roads surface (which feature a strong dependence on the weather and precipitation level) [11, 12]. It was observed that soot and organic aerosols have small diameters in the range of PM2.5 meanwhile mineral particles are rather situated in PM_{10} range.

The road dust induces air floating particles due to the interaction with the moving cars [13, 14]. An important source of minerals in the dust is the asphalt and the road shoulder erosion at the contact with the car tires [12]. The breaking procedure enhances the abrasion, which increases with the friction coefficient. Anti – skid material is often used to adjust the road friction coefficient during the winter. This granular material acts as a rough dust between the tire and the road surface. It is subjected to an average grinding in such condition affecting its structure, certainly being able to release fine mineral fractions. These are incorporated into the road dust and further suspended in the air [12].

Similar study evidence the re-suspension tendency for the sedimenting particles on the adjacent snow layers due to their small size which are very sensitive to a significant modification of air velocity [14, 15]. The re-suspension process act mainly due to the lower cohesive forces observed for the fine particles which are lifted up by ascension force. Such mechanism could increase the PM_{10} and $PM_{2.5}$ air level during winter when is expected to be lower than in summer.

The anti skid material prove to be a major pollution source during winter. All mention aspects reveals that the mechanical behavior of the anti – skid material under traffic condition is the cause of pollution increasing. Such properties are directly influenced by the chemical composition and particle dispersion. The aim of present paper is to analyze the composition of anti-skid material used in Cluj-Napoca and to identify it’s components in the PM_{10} and $PM_{2.5}$ emissions.

RESULTS AND DISCUSSION

AM contains two kinds of components: silica particles (mended to increase the friction coefficient between cars tires and road surface) and an anti – frost agent to prevent the glaze formation (usually sodium chloride is used).

The collected AM samples have a composition based on silica particles ranging from 1 to 10 mm. The total mineral amount represents 80 % and the rest of 20 % is the sodium chloride as anti – frost agent. A closer observation of the collected samples evidence silica particles having rounded shape and some intriguing brown particles (rusty like) having an unknown nature. They seem to be mineral conglomerates with a complex microstructure.

Sodium chloride particles are crystallized in cubic system featuring large crystals having cubic and octahedral particles as typical forms related to the BCC structure.

The mineral composition of AM sample was determined by XRD spectroscopy. The AM particles were grinded in a ball mill to obtain a powder suitable to be subjected at XRD investigation. The obtained diffractogram is presented in Figure 1a.

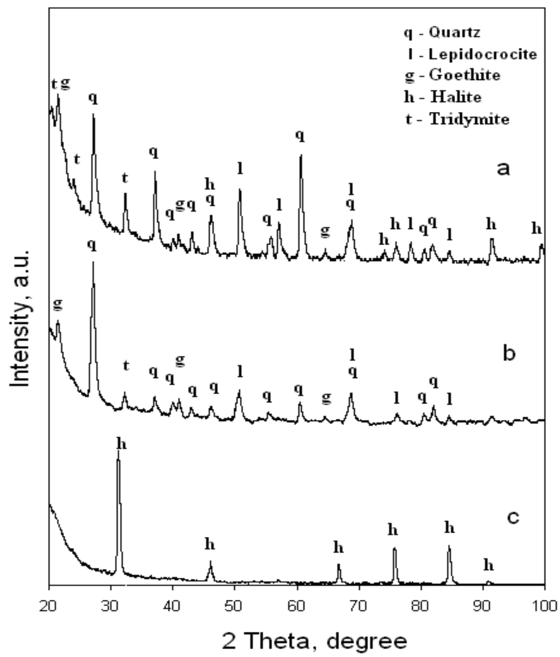

Figure 1. The X - ray diffraction spectrum for the investigated anti-skid material: a) grinded non skid material, b) grinded iron hydroxide particles and c) halite particles.

It features well developed peaks related to the crystalline state of the sample. The dominant mineral found in the composition is quartz, having the most intense peaks. Sodium chloride was identified as crystalline halite. Each component amount was appreciated based on the XRD peaks relative intensities related to its structure factor. All identified components of AM sample are listed in Table 1 as well as their amount in the sample and their optical features in cross polarized light.

The significant presence of Tridymite (an allotrope of quartz) is sustained by it's presence in common river sand in Romania due to the sedimentation condition [16, 17]. Moderate quantities of tridymite found in silica granular material is a collateral evidence that the gravel used in the investigated anti skid material is dug up into a local gravel - plant (e.g. Harghita county – due to the proximity to the Sf. Ana volcano). Quartz has a hexagonal compact crystal lattice meanwhile trydimite is orthorhombic (it derives from quartz by intensive heat treatments as found in volcanic eruptions. Both quartz and tridymite particles feature a light green gray aspect in cross polarized light, Figure 2a. Their morphology is derived from broken silica spherical particles. It features several rounded particles mixed up with broken ones having sharp edges crossed at small angles.

Table 1. Components properties of AM sample

Component	Quartz	Lepidocrocite	Goethite	Halite	Tridymite	Total
Wt.%	60	10	8	10	12	100
Particle size range, μm	30 - 250	10 - 250	10 - 250	30 - 500	30 - 250	-
Color in cross polarized light	Green-gray	Reddish-brown	Reddish-brown	Pale white	Green-gray	-

The most interesting findings in AM are the iron hydroxides in crystalline form of: lepidocrocite and goethite. In figure 2a appears as brown particles having 30 – 50 μm. Their presence in AM sample proves to be related to the intriguing brown particles observed at macroscopic analysis. Therefore, we separated from the AM sample a significant number of rusty particles as well as a significant number of halite. Each category was crushed separately and resulted powders were investigated by XRD. The obtained spectra are presented in figure 1b and 1c.

Even more intriguing is the results of rusty particles composition. The major component over 65 % is the mixture of lepidocrocite (γ – iron hydroxide) accompanied by its allotrope goethite (α – iron hydroxide). The surprise is the evidence of quartz (35 %). It is really an interesting quest: how could be explained such composition revealed for the rusty particles. Some evidences to reveal the mystery was found in the mineralogical microscopy performed with cross polarized light on the rusty particles powder, Figure 2b. It appear to be a refined mixture of quartz slivers having 20 – 30 μm (some of them presents rounded shape due to their log proliferation in open environment and some are fresh broken featuring sharp edges). The iron hydroxides act as a binder of quartz slivers. It is possibly in condition of road traffic.

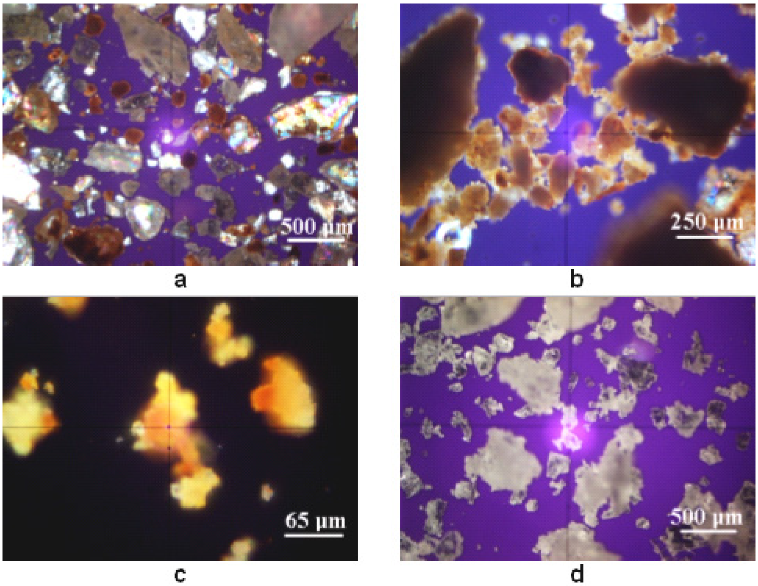

Figure 2. The cross polarized light microphotographs:
a) broken anti-skid material particles, b) broken iron hydroxide particles,
c) fine fractions of iron hydroxide particles, and d) halite particles.

A more detailed view catch some individualized iron hydroxide particles, figure 2c, having diameters between 10 – 50 μm. Their appearance is agglomerated, sustained the ability as mineral binder in relative humid environment.

The quartz particles from the street dust physical interacts with the car cassis rust in presence of anti skid material and relative humidity typical for winter and forms micro aggregates like those observed in Figure 2b. Considering several cycles of coalescence between micro aggregates finally results macroscopic particles such those observed in AM sample. This is a major fact which proves that AM sample contains re-circulated anti skid material re collected from the road sides. The implication for environment could be important even is able to become an environmental hazard.

Sodium chloride extracted from AM sample was also subjected to XRD. It reveals peaks only for halite, proving its high purity. The micro-structural aspect is presented in figure 2d, a fine mixture of cubs and octahedral crystal forming domains with polyhedron shape. Hence, sodium chloride is very solvable in aqueous or humid environment it is not a problem to interfere with air particulate matter suspensions.

The compression test results shows broking strength of 2054 MPa for silica particles and 840 MPa for iron hydroxide conglomerate. Silica particles compression strength strongly depends on the flawless structure. The values are in good agreement with the data in literature [18]. It proves that quartz particles have a good quality and are more resistant at mechanical solicitation than the other particles found in AM. Particularly, the iron hydroxide conglomerate feature small quartz slivers in composition, fact observed in Figure 2b. They act as cracking promoters reducing the compression strength as well as the particle cohesion.

Considering the interaction between car tires and road surface it exhibits local solicitation higher than 1000 MPa, fact which leads to the inevitable disintegration of rusty particles. Furthermore, the silica granules from anti – skid material acts as milling bodies refining the size of iron hydroxides as well as quartz slivers. Figure 2 b and 2c gives us some dimensional clues that fine particle could result after disintegration process. It needs to be considered diameters such 1, 2.5, 10, 20, up to 50 μm. All sizes range could be easy generated by automotive traffic.

The decaying of rusty particles in winter condition under pressure leads to the formation of fine particles below 10 μm diameter. The evidence of disintegration at microscopic level was traced out by dispersing the milled powder in deionized water under intensive agitation. Thin layer of particles were transferred on glass slide by immersion in the agitated dispersion for 30 seconds, followed by natural drying. The glass slide was microscopically inspected under cross polars and the resulted images are presented in Figure 3a. The iron hydroxide particles are very abundant, many of them features diameters around 20 μm but there are several finest particles in the range of 1 – 10 μm. All these fine micro - particles are able to be floated by air currents along the roads formed by automotive traffic [13, 14].

The thin layer was also subjected to XRD. Resulted a pattern is very similar with the one in Figure 1b. It proves that lepidocrocite, goethite and quartz slivers are able to form individualized PM_{10}; $PM_{2.5}$ and floating – sedimentable particles into the atmosphere. The data in literature state that any material particles spreaded or abandoned on the street are enclosed in the common street dust, and after is subjected to the air re-suspension [12, 15]. If so, we expect to found in winter atmosphere some other minerals belonging to the street adjacent environment decaying (e.g. clay mineral and perhaps calcite, very often found in the ground in Cluj-Napoca).

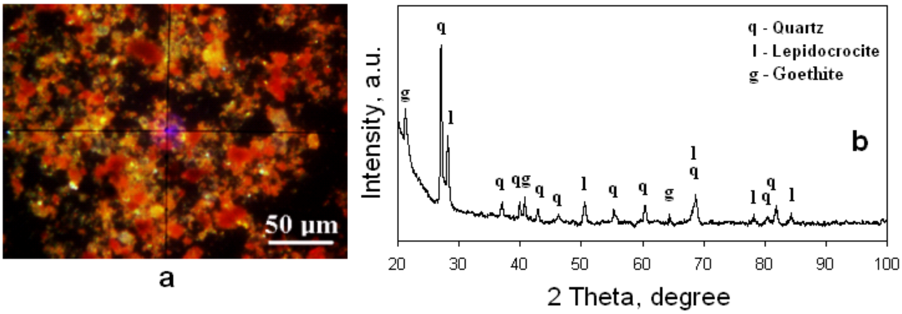

Figure 3. Thin layer of rusty particles powder transferred on glass slide via aqueous dispersion: a) cross polarized light microphotograph and b) XRD pattern.

Therefore, we collected particulate matter samples from atmosphere for the most representative winter months (December 2011, January 2012, and February 2012). The sedimenting particles (SP) collected were subjected to the XRD analysis. Resulted spectra are presented in Figure 4. Each of them present very well developed peaks proving the high crystalline state of the samples. The composition is the same for all three samples. The average characteristics are centralized in Table 2.

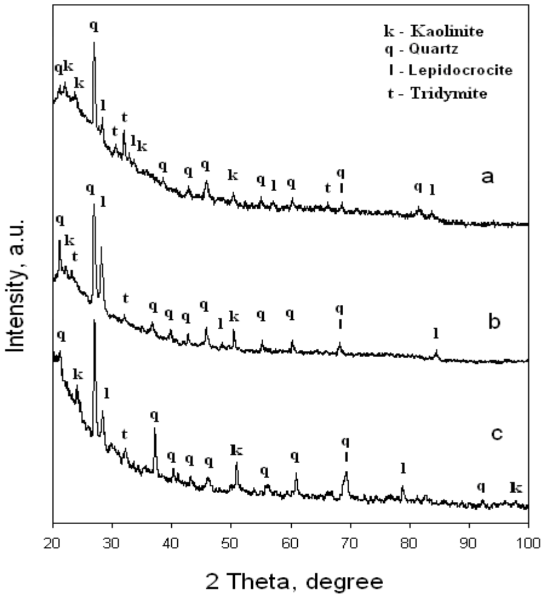

Figure 4. The X - ray diffraction spectrum for the sedimentable particles collected from air: a) December 2011, b) January 2012, and c) February 2012.

Table 2. Components properties of SP sample

Component	Quartz	Lepidocrocite	Kaolinite	Tridymite	Total
Wt.%	70	15	10	5	100
Particle size range, μm	1-30	1-30	1-10	1-30	-
Color in cross polarized light	Green-gray	Reddish-brown	Blue-white	Green-gray	-

Note: some isolated micro – particles could exceed 50 μm diameter

Microstructure of the sedimenting particles collected in December 2011 contains well dispersed fine microscopic particles. The cross polarized light inspection, Figure 5a, reveals a mixture of fine quartz particles together with lepidocrocite, kaolinite and tridymite. The detail at high magnification presented in Figure 5b, reveals better the shape and size of the minerals involved. The dimension ranges as well as mineral color in polarized light are centralized in Table 2. Similar observations were found for the SP samples collected in January 2012 and February 2012, the mineralogical microscopy results being displayed in Figure 5 c - f at average and high magnification.

Caolinite presence in the SP composition is interesting during winter because it is a clay mineral which belongs to the street adjacent areas. Its presence in the street dust is more signaled in summer [13]. The winter condition with snow and frost areas inhibits the decaying of street adjacent areas (the top ground is frost no particle is able to move under air currents). Still, a kaolinite amount of 10 % could be usual in winter considering the remains incorporated in street dust in autumn.

Quartz found in SP samples has two sources during winter: the soil decaying remains and the quartz slivers resulted from disintegration of rusty particles found in AM sample. It is the dominant mineral representing 70 % of SP average composition. But, the major prove of air disperse particulate maters generated by the anti – skid material is the presence of lepidocrocite at 15 % amount. Its particle size varies in a range of 1 – 30 μm as can be observed in Figure 5 b, d, and f. The evidenced range contains the most hazardous air particulate matters such $PM_{2.5}$ and PM_{10}.

The tridymite presence in SP samples as traces (over 5 %) also proves of particulate emissions caused by anti –skid material. In the real condition the multiple interactions between car tires and road surfaces intermediated by AS sample leads also to degradation of silica particles, some of them being crystallized as tridymite. The bilateral shock compression during car braking could promote cracks along silica crystal imperfection favoring the particle disintegration.

An amount of 15 % lepidocrocite was found in SP sample. It was induced in atmosphere by the same way as quartz slivers. Mineralogical microscopy evidence a lot of lepidocrocite particles in the range of 1-10 µm, sizes able to be incorporated in the $PM_{2.5}$ and PM_{10} emissions. It is interesting that goethite do not appear in SP sample. It is possible that goethite fine particles exposed for a long term to the winter environmental condition to transform themselves into lepidocrocite via natural decaying [19 – 20].

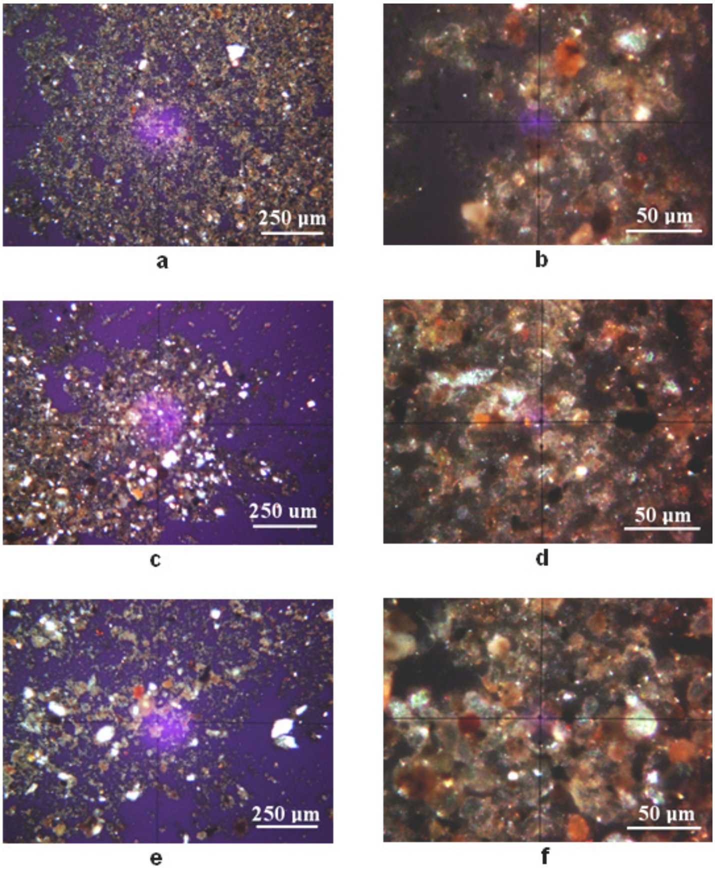

Figure 5. The cross polarized light microphotographs – different magnifications: a,b) December 2011, c,d) January 2012, and e,f) February 2012.

The particulate matter emissions were also quantitative measured using the Automatic Monitoring Air Quality Stations in the custody of Environmental Protection Agency of Cluj. Achieved data were centralized in Table 3.

Table 3. Particulate matter emissions data

Emission type		December 2011	January 2012	February 2012
$PM_{2.5}$, μg/m^3	min.	2.17	2.90	6.53
	max.	47.50	64.73	53.85
	average	28.19	23.50	35.23
PM_{10}, μg/m^3	min.	2.72	5.25	9.25
	max.	49.32	52.76	52.58
	average	27.37	19.95	31.33
SP, g/m^2/month	average	5.73	5.97	6.02

$PM_{2.5}$ emissions average value ranges from 23.50 to 35.23 μg/m^3 for all monitoring period. The risk level is low, because the average value is far away from the maximum limit. However, in days with high automotive traffic were signaled slightly exceeds of the limit: in 31 January 2012 was registered a peak of 64.73 μg/m^3 (an excess with 14.73 μg/m^3); and in 23 February 2012 was registered a peak of 53.85 μg/m^3 (an excess with 3.85 μg/m^3). The slightly exceeding mentioned is caused by the conjugated effect of intensive car traffic with presence of anti – skid material on the road surface.

The same variation could be observed for PM_{10}, Table 3, the average values are really lower than the accepted limit. The fact sustains that the environmental risk is low. However the PM_{10} maximum registered exceeds the limit with: 2.76 μg/m^3 in January 2012, and with 2.58 μg/m^3 in February 2012 at the same days reported for $PM_{2.5}$. The SP emissions are in a good range, below the maximum limit of 17 g/m^2/month, no exceed were registered. Overall, the environmental risk is very low, because the average value is far away from the maximum limit.

A proper street management could reduce the effect of AS material related particulate matter emissions by an adequate sorting of re-circulated anti –skid material.

CONCLUSIONS

Anti – skid material investigated in present study contains silica particles (e.g. quartz and trydimite) to increase the friction coefficient between cars tires and road surface and halite (sodium chloride) as anti glaze agent. Some interesting rusty particles were found in the anti skid material used in Cluj-Napoca in the 2011 – 2012 winter. The XRD and mineralogical microscopy analysis found that their composition is a micro-structured mixture of iron hydroxides (e.g. lepidocrocite and goethite) with fine quartz slivers. Compression test shows a good strength of silica particles of AM and a low strength for rusty particles. These ones are mechanically disintegrated by the force action between car tires and street surface. Silica particles having a higher strength act as milling bodies of the rusty particles. We milled some of rusty particles and the resulted powder was dispersed in deionized water. Aqueous dispersion evidences the formations fine fraction in the range of 1 – 10 µm. The particulate matter samples collected from air from December 2011 to February 2012 proves the incorporation of lepidocrocite and quartz slivers from anti skid material. Lepidocrocite amount reached in SP sample is situated at 15 %. The results of monitoring performed with Automatic Monitoring Air Quality Stations prove that the emissions are directly increased with the car traffic on the Aurel Vlaicu Street. The average values for PM2.5, PM10 and SP are below the maximum accepted limit, so the risk level is low. Finally, we can conclude that a better management of anti skid material could be improved to reduce the particulate matter emission during winter by a proper sorting of re-circulated anti skid material.

EXPERIMENTAL SECTION

Anti skid material samples were collected in the 2011 – 2012 winter from the distribution points around Aurel Vlaicu Street in Cluj-Napoca, Romania. Equal quantities of anti skid material were mixed together to obtain an average representative sample (AM). AM sample was further grinded in a ball mill to obtain a mixture of broken particles which are suitable for physic and chemical analysis.

The particulate emissions into the atmosphere were monitored with Aurel Vlaicu Air Station. There were collected from air monthly samples of sedimentable particles (SP) via wet deposition for December 2011, January 2012, and February 2012. The SP dispersion was dried by evaporation, resulted powder was considered for analysis in present paper. PM_{10} and $PM_{2.5}$ were also monitored for the area of interest using the Automatic Air Quality Monitoring stations driven by Environmental Protection Agency of Cluj.

Mineralogical composition was elucidated by XRD spectroscopy using a DRON 3 diffractometer equipped with data acquisition module and Matmec IV.0 soft. The XRD spectra were obtained using a Cu k_{α} radiation. Mineral were identified from XRD patterns using Match 1.0 identification soft powered by Crystal Impact Company and PDF2 (Powder Diffraction File database second edition).

Particles size and morphology were investigated using the mineralogical microscopy with cross polarized light, using a Laboval 2 microscope produced by Carl Zeiss Jena. Digital capture was performed with a Samsung Camera having 10 Mpx. The special microscopic interpretation and particles measuring were developed using Image J 1.40g soft as a free resource provided by National Institute of Health of USA.

Compression tests were performed on a standard compression machine registering the broken pressure at compression for some of the particles within the anti skid material.

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