



CHARACTERIZATION OF AIRBORNE PARTICLES AND SOURCE IDENTIFICATION USING SEM/EDS

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Samples of particulate matter were collected during the winter season from the urban area of Tirana, Albania. Qualitative analyses of particulate matter were performed using Scanning Electron Microscope (SEM) coupled with high Energy Dispersive X-Ray Spectrometer (EDS). Based on chemical analysis and the morphology (the size and shape of particles), the most abundant groups in all sampling days were aluminosilicates (fly ash and soil particles), calcium rich and carbonaceous particles. Air mass trajectories show the presence of Saharan dust during 80 % of sampling days.

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Introduction

Suspended particulate matter is one of the major air pollutants affecting human health.^{1,2} Sources of particulate matter are both natural and anthropogenic. Aerosol particles are complex and heterogenic from their physical characteristics, chemical composition, and origin, and have toxic effects on human health. Depending on particle dimensions they remain suspended for long time enough to penetrate into the respiratory tract.³⁻⁶ The physical and chemical characteristics of particles are different, due to large variability of emission sources, and formation and post formation processes. Information about particle size, shape and elemental composition are essential to understand the contribution of emission sources. These data cannot be taken from chemical analysis only. Scanning Electron Microscopy (SEM) coupled with energy dispersed X-ray spectroscopy (EDS) provides a powerful tool for the physico-chemical characterization of particulate matter. Several environmental studies have been carried out for the characterization of airborne particulates and their source apportionment using SEM/EDS techniques.⁷⁻¹⁴

This study aims the characterization of particulate matter in Tirana. Due to rapid urbanization and demographic movement toward Tirana city, about 27 % of the population in Albania lives in Tirana. With a population density of 454 inhabitant/km² and about 88.6 % urban population,¹⁵ the pressure on the environment is very high and the city of Tirana is facing serious problems of air pollution. Vehicles fleet in Tirana is mostly private cars using diesel fuel. Tirana has Mediterranean climate with annual average temperature of 16 °C. It is located in Central Albania and is mostly covered by hills. Geological formations in Tirana area

include coal, quaternary sediments, clays, limestone, quartz sand, schist, conglomerates, volcano sedimentary formations and bauxites.

Materials and methods

Sampling

Samples of suspended particulate matter were collected at the second floor of four storey building of the Faculty of Natural Sciences (Figure 1). This building is located alongside with Zogu I Boulevard, a busy traffic street, and near a busy intersection with heavy traffic. A low volume sampler (Escort ELF air pump) was set to operate at 3 L min⁻¹ for air sampling. Suspended particles were collected on Sartorius nuclepore polycarbonate filters having a diameter of 37 mm and 0.45 μm pore size. Each sample was collected continuously for twenty four hours to prevent overloading and formation of secondary aerosol particles due to the recrystallization process. Particulate matter sampling was carried out from 16 January to 25 January 2014 and a total of 7 samples were collected for analysis. Filter samples were weighed before and after sampling time using a microbalance. TSP mass concentrations were measured gravimetrically. Collected samples were put in plastic cassettes and stored until analysis time in the laboratory at 25-30 °C and relative humidity under 50 %.

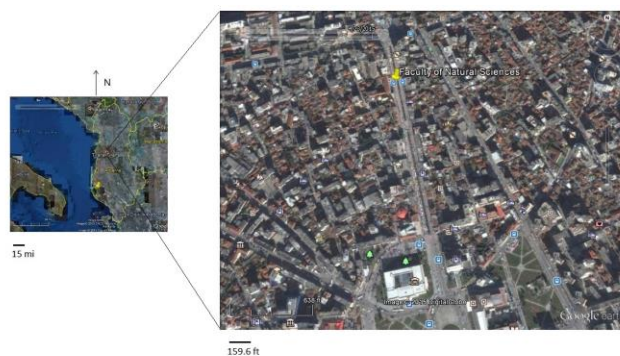


Figure 1. Location of sampling site.

SEM-EDS analysis

Individual characterization of aerosol particles was performed using scanning electron microscope JEOL JSM-5600 equipped with an Oxford Link ISIS L300 for EDX analysis, at the Department of Chemistry, University of Ioannina, Greece. SEM/EDS analyses were performed according to EPA Guidelines¹⁶. Sections 5 mm by 5 mm of filters were cut from each sample and mounted with a carbon film on aluminium SEM stubs for analysis. The working conditions of accelerating voltage of 20 kV, probe current under 100 μA and 21 mm working distance were set. To provide representative results and minimize subjectivity, the results were taken from three randomly selected fields for each filter examined. Each of the particles within a field was analyzed. Manual SEM particle examinations were carried out at magnifications up to 8000 and secondary electron images were acquired. EDX spectra for the centre of particles on SE images with energy range of 0-20 keV and count rate 5-89 cps with approximately measuring time of 100 s were accumulated. Agglomerates with variable chemical composition present in PM samples were examined in different parts. All photomicrographs of individual particles and EDX data were collected for particle classification. Chemical elemental analyses were performed for C, Ca, Al, Si, Cl, Na, K, P, S, Mg, Fe, Cr, Cd, Mn, Pb, Cu, Ti, Zn, Ni, Cs and Co.

Backward trajectories

In order to analyze the sources and transport of aerosol particles at the sampling site, the air mass backward trajectories were calculated for the sampling period. Isobaric backward trajectories were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and the meteorological data of NOAA Air Resources Lab. website (<http://www.arl.noaa.gov/ready/hysplit4.html>). The calculation method of NOAA HYSPLIT model is hybridization between Lagrangian and Eulerian methods.¹⁷

Five-day backward trajectories, during sampling period, were calculated for 500 m, 1000 m and 1500 m above the ground level ending at 06:00 UTC, corresponding to the changing time of the filters, and are presented in the Figure 2. The results show the dominance of long trajectories (80 % of the sampling days) that start from the Sahara desert and Mediterranean Sea and arriving in Tirana at low latitudes, smaller than 1000m, where aerosol concentrations are commonly high. Many studies have shown that air masses from Mediterranean Sea transport aerosols from different continental sources and are rich with Sahara dust.^{18,19}

Analysis of backward trajectories of air masses for specific days show the presence of air masses from Sahara (Sample S3) and Central Mediterranean region (Sample S2 and S6) and reflect the transport of aerosol particles with natural origin. The samples S4 and S5 are influenced by air masses from Western Mediterranean air masses passing over the South of Italy which can transport both aerosols with anthropogenic and natural origin. The sample S1 is influenced by air masses from North Adriatic and S7 is influenced from air masses from Peloponnese area of Greece, suggesting the transport of continental aerosol particles with anthropogenic origin.

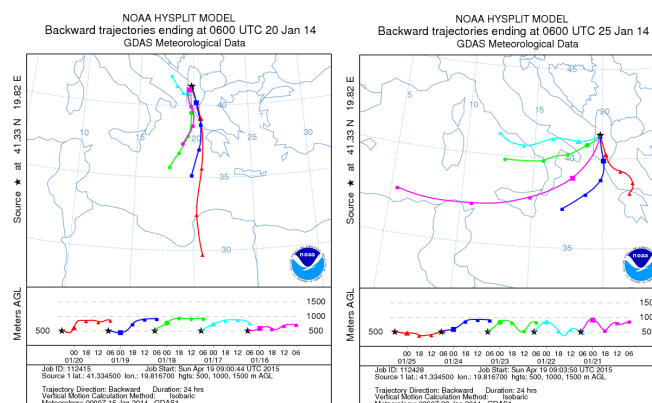


Figure 2. Five-day air-mass backward trajectories at 500, 1000 and 1500 m AGL latitudes, ending at 06:00 (UTC), for the sampling days: a) 16-20 January 2014, b) 21-25 January 2014.

Results and Discussions

Table 1 gives sampling dates and TSP mass concentrations. The mean TSP mass concentration ranged from 56.42 $\mu\text{g m}^{-3}$ to 98.46 $\mu\text{g m}^{-3}$. Meteorological data during the study period were provided by Meteo Tirana station located in Tirana (N 41° 18' 55"; E 19° 48' 55" and elevation 404 m). During the study period calm conditions and wind directions blowing out from the south to east were dominant.

SEM images of particles showed a wide range of particle sizes and shapes. According to their size, shape and elemental composition 650 particles having a physical diameter greater than 0.5 μm were analyzed. According to the diameter size, the dominant particles corresponded to the fine fraction (smaller than 2 μm). A very small number of particles having a diameter between 10-20 μm were detected. Based on individual particle X-ray spectra performed by EDS the most abundant elements detected were Ca, C, O, Si, Al, Mg, Mn, Pb, Fe and Cd, present in both coarse and fine fractions. Other elements such as Na, K, P, S, Ti, Cs, Ni and Cr were present in minor amounts in the most of the particles.

Based on their morphology and chemical analysis two main particle classes were detected, natural and anthropogenic. Natural particles consist mostly soil dust (minerals) and biogenic (biological fragments, spores, pollen, fungi, etc) particles. Soil particles have irregular shapes and rough surfaces and sometimes form aggregates with irregular shapes and sizes, while biogenic particles were highly structured, with rounded shapes and smooth surface. Anthropogenic particles emitted from combustion processes were predominantly spherical and rounded with smooth surface. The most abundant particles were classified into 7 groups in the decreasing order, aluminosilicates (fly ash and soil particles), Ca-rich particles, carbonaceous particles (soot aggregates and biological particles), mixed particles, Si-rich, Fe-rich and aged sea salt particles.

Table 2 gives a summary of particle groups, corresponding relative abundances, elemental composition and their morphology characteristics for total examined samples.

Table 1. A summary of sampling data

Samples	Sampling date	TSP, $\mu\text{g m}^{-3}$	Weather conditions			
			Wind speed (m s^{-1})	Wind direction	Temperature, $^{\circ}\text{C}$	Relative humidity, %
S1	16-17/01/201	64.17	0.41	SSE	11.4	85
S2	17-18/01/201	75.35	0.5	SE	11.6	75
S3	19-20/01/201	81.68	1.2	SE	9.1	66
S4	20-21/01/201	98.46	1.36	ESE	6.3	83
S5	22-23/01/201	72.63	0.83	SE	6	89
S6	23-24/01/201	56.42	0.72	SE	10.3	84
S7	24-25/01/201	61.39	0.61	SE	10.6	84

Table 2. Particle groups of particulate matter from 16 January to 25 January in Tirana

Particle groups	Abundance, %	Subgroups	Elemental composition	Morphology
Aluminosilicates	13	Si- Al- / Fly ash	Si and Al dominant, moderate amounts of Fe, with Na, Mg, Ca, P and S content	Spherical
	30.2	Si- Al- Ca/ Soil	Dominant Si, Al and Ca with moderate amounts of Fe, Mg and Cr; minor amounts S, Co, Ni, Cu and Pb	Irregular
Ca-rich compds.	19.6	Calcite (CaCO_3)	Ca dominant with minor amounts Al, Si, Mg, S and K	Irregular
		Ca-Mn-Pb	Ca, Mn and Pb dominant; variable amounts of Al Mg, Na, Mg, Si, S and Cd, trace of Cs, Cr, Fe, Co Ni and Cu	Irregular
		Ca-Mn-Mg-Al	Ca, Mn, Mg and Al dominant; variable amounts of Na, Si, S and Cd, trace of Cs, Cr, Fe, Co Ni and Cu	Irregular
		Ca-Cd	Ca and Cd dominant; minor amounts of K, Si, Al, Mg, P, and S; trace metals Cr, Fe, Co Ni and Cu	Irregular
Soot	11.5	C-O	C content higher than O	Aggregates
Biogenic	8.7	C-O	C and O in the same amounts and N, P, Cl and S contents	Well-defined
Si-rich	4.1	Si-O	Si dominant variable amounts of Al, Na, Mg and trace of S, K and Ca	Irregular and rounded
Fe-rich particles	1.6	Fe-O	Fe dominant with traces of Na, Mg, Al, Si, K Ca, Cr, Mn, Co and Zn	Irregular and rounded
Aged sea salt	1.1	Na	Na and S with contents of Mg, K, Cl, Si and Cu	Irregular
Mixed particles	10.2	Variable components	Variable combination of Ca, Si, Al, Mn, Cd, Pb, Mg and Fe with trace of P, S, Na, Cu, Co and Ni	Irregular

SEM photomicrographs and respective EDX spectra of the typical particles, which are described in detail with regard to their characteristics, are shown in Figure 3.

Relative number abundances (%) of the particle groups on different sampling days are shown in Figure 4. Both Figure 2 and Figure 4 clearly demonstrate the dependence of the chemical composition of particulate matter on the trajectory of air masses.

Aluminosilicates (43.2 % relative abundance), divided in two subgroups, fly ash and soil particles, were the most abundant particles. They are characterized by high amounts of both Si and Al, moderate amounts of Fe, variable combinations of Ca, Mg, Na, P, S, Ti, and other metals in

trace amounts. Aluminosilicates with spherical shapes (Figure 3a) were characterized as fly ash particles and were present in all examined samples. Fly ash particles were distributed mainly in the size range of 1-5 μm . They come from anthropogenic source and can be produced by different combustion processes. These particles consist 30.4 % of aluminosilicates group. Sample S3 (weekend day) is less abundant with fly ash, 9.6 % of aluminosilicates and 4 % of all particles analyzed in this sample. All the other samples taken during weekdays have closely relative amounts of fly ash particles. These results reflect the influence of traffic emissions as major source of fly ash particles. Soil particles with irregular shapes (Figure 3b) were dominant ones within the aluminosilicates group (56.1 %). A part of these particles are seen as aggregations of smaller particles rich in Si, Al

and Fe. They come from soil, and in urban atmosphere may be derived mostly from resuspension of road dust caused by vehicles or carried by air masses.²⁰

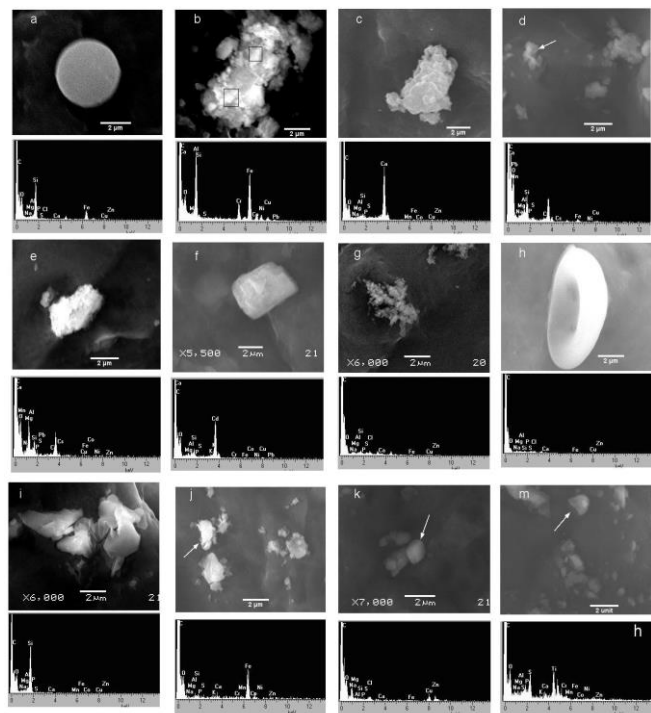


Figure 3. SEM photomicrographs and respective EDX spectra for: aluminosilicates- a) fly ash particles, b) soil particles; Ca-rich particles- c) calcite (CaCO_3), d) Ca- Mn- Pb particles, e) Ca-Mn-Al particles, f) Ca-Cd particles; Carbonaceous particles- g) soot aggregates, h) biogenic particles (pollen or spore); i) Si-rich (natural quartz particles); j) Fe-rich mineral particles; k) aged sea salt particles; m) mixed particles.

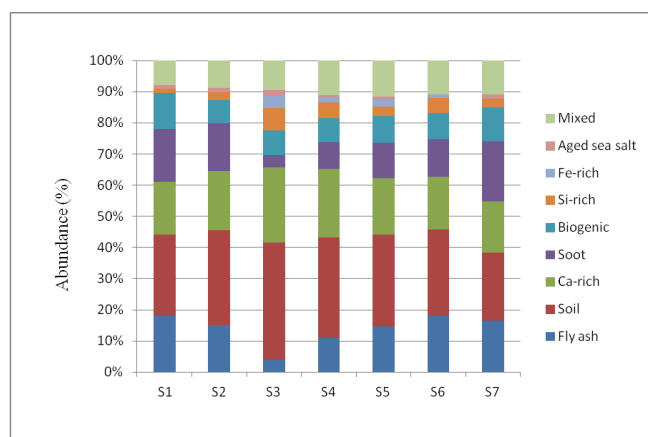


Figure 4. The relative number abundance (%) of the particle groups on different sampling days.

These particles can also contain much higher ratio of potentially anthropogenic phases (amorphous phases, salts, magnetite), while they can be hidden by the large amount of coarse particles of soil origin.²¹ The Figure 4 shows that all samples are dominated by soil particles but, the samples S3

and S4 are largely dominated. Soil particles consist 37.6 % and 32.2 % of all analysed particles and 91.4 % and 74.5 % of aluminosilicate group particles in the samples S3 and S4 respectively, reflecting the influence of Saharan dust in particulate matter in Tirana.

Ca-rich particles (19.6 % abundance) group was the second most abundant, in the range from 16.4 % (S7) to 24 % (S3). The major part of this group is made up by calcite particles, which are dominated by Ca (> 60 %) with minor amounts of Al, Si, Mg, S and K (Figure 3c). These particles were present in all aerosol samples. They result mainly from geogenic origin and are composed of carbonate minerals including calcite and dolomite^{7,13}. Calcite particles (CaCO_3) can be generating from lime production, cement manufacturing and building construction. These particles can also come from the rocky hills which form the background of Tirana. Particles such as Ca-Mn-Pb (Figure 3d), Ca-Mn-Mg-Al (Figure 3e) and Ca-Cd (Figure 3f) are included in the group of calcite particles. Particles rich in Ca, Mn and Pb were found in fine fraction and contained minor amounts of Al, Na, Mg, Si, S, Cd and trace of Cs, Cr, Fe, Co, Ni and Cu. The analysis of shape cannot yield any information about the possible source. The airborne Ca particles are mainly derived from earth crust. Pb is typically derived from anthropogenic combustion processes such as the use of leaded gasoline, coal combustion or may be the use of paints and plasters during construction activities. Mn is a metal of both natural and anthropogenic origin. Mn may be derived as one of additive elements in gasoline or is naturally occurring in many types of rocks. The presence of Ca, Pb and Mn in moderate amounts indicated that these Ca-rich particles cannot come from traffic emission. These particles were present only in the samples S3, S4 and S6, suggesting that may be from Saharan dust. Some authors have suggested that lead concentration in soils can be seen as tracer of the potential anthropogenic contamination occurring during Saharan aerosol transport and fallout.²²

Soot aggregates (11.5 % abundance) are composed by spheres with diameter smaller than $0.1 \mu\text{m}$, and the C content is higher than O and are thus easily distinguished from other particles. These particles are of much interest because these are considered as second largest contributor to global warming. They may originate in different ways from incomplete combustion of gasoline, oil, diesel and other fuels, being so these are good tracer of vehicle emissions.²³ SEM photomicrographs and respective EDX spectra for soot aggregates are presented in the Figure 3g. The variation on different days of soot particles like fly ash particles suggests that its major source is traffic related. Few particles can be attributed to the combustion of fossil fuels for domestic heating.

Biogenic particles (8.7 % abundance) are the most easily identified among other particles and include a wide range of spores, pollens, bacteria, fungi and fragments of plants and insects. Biogenic particles contain C and O in the same amount and minor amounts of P, Cl and S. They were present in all samples and were indifferently distributed on sampling days. These particles of natural origin are seasonal dependent. They have highly structured and symmetrical shape and different sizes mainly in coarse fraction. SEM photomicrographs and respective EDX of typical biogenic particle are shown in Figure 3h.

Si-rich (4.1 % abundance) particles, classified as quartz (Figure 3i), contain predominately silicon (SiO₂). They also contain variable amounts of Al, Na, Mg, P and traces of S, K and Ca. More than 60 % of these particles were found in coarse fraction. The major part (55.5 %) of all Si-rich particles was observed in two samples, S3 and S4. They can be derived from soil and carried by wind or from construction activities and transported materials.

Fe-rich particles (1.6 % abundance) may be of both anthropogenic and natural origin. They contain mainly Fe with traces of Na, Mg, Al, Si, K Ca, Cr, Mn, Co and Zn. Fe-rich particles were absent in the samples S1, S2 and S7. Very few irregular Fe-rich particles from soil origin were detected, their diameter is mostly smaller than 5 µm (Figure 3j).

Aged sea salt (1.1 % abundance) particles differ from fresh sea salt of marine aerosol. These particles contain mainly Na with some amount of Mg, S and K and traces of Cl, Si, Cu and Zn. The crystals of fresh sea salt undergo chemical and morphological changes during the long transport, especially depleting Cl content of particles and driving it into the atmosphere.^{24,25} Detected aged sea salt particles were found to be rounded or well-shaped (Figure 3k). They come from Mediterranean air masses.

Mixed particles (10.2 % abundance) contain variable combination of Ca, Si, Al, S, Ti, Mn, Cd, Pb, Mg and Fe. These particles, which could not be classified as one of described groups, were mostly in the fine fraction and with rounded shape. They may be either from mineral origin transported by winds or anthropogenic origin such as construction activities, tire wear debris and abrasion of different materials. Another source can be direct traffic emissions mixed with road dust resuspended several times. An example of mixed particles is presented in Figure 3m.

Conclusions

Gravimetric measurements show that the mean TSP mass concentrations range from 56.42 µg m⁻³ to 98.46 µg m⁻³. The air mass backward trajectories indicate that urban atmosphere of Tirana during the sampling period was affected by Saharan dust event and air masses from Mediterranean Sea. The conduction of SEM/EDX analysis provided information on individual particle morphology and chemical composition, important characteristics to assess the contribution of major sources to the particulate matter. Morphology analyses of individual particles show that nonspherical particles of crystal origin were dominant in all dust samples. For all samples, both in the fine and coarse fractions, predominant elements were Si, Al, Ca, and variable amounts of Fe, Mn, Pb, Cd and Cr. These results confirm the influence of Saharan dust of particulate matter composition in urban atmosphere of Tirana. For the sampling period, two major sources of particulate matter affect urban atmosphere in Tirana, anthropogenic and natural sources. Anthropogenic emission sources include traffic emissions, resuspended road dust induced by traffic and construction activities. Natural sources include mineral particles of local origin and carried by air masses over Mediterranean region mainly from Saharan dust origin.

With extended data and further statistical analysis the source apportionment can be clarified.

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