Physicochemical characterization of Atmospheric Particles $PM_{2.5}$ using Chemical Microanalysis Methods

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***Abstract* - The experimental study and determination of concentration, size and morphological characteristics of particles are necessary for clarification of their impacts on human health and climate changes. Sampling of $PM_{2.5}$ and PM_{10} has been carried out at National Technical University campus in Athens by using TCR Tecora (Sentinel PM) samplers and PTFE filters, time-programmed to operate in parallel at the same point from May 21st to 7 June 2014. Daily atmospheric concentrations have been determined by gravimetrically and concentrations of the water soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) by ion chromatography. The particles morphological characteristics and their chemical composition were determined by Scanning Electron Microscopy and Energy Dispersive X ray analysis (SEM-EDX). The results obtained permitted the comparison between $PM_{2.5}$ and PM_{10} with respect to their physicochemical characteristics and their origin after wind roses and back trajectories evaluation.**

Keywords: Particulate Matter, Secondary Inorganic Aerosol, Saharan Dust, Back Trajectories, SEM-EDX analysis.

I. INTRODUCTION

Atmospheric particulate matter in urban environments is considered one of the highest priority pollutants for which legislation is becoming more stringent: $PM_{2.5}$ annual target value is set at 25 μg/m^3, not to be exceeded for more than 35 days in a calendar year while for PM_{10} the daily target value is set at 50 μg/m^3, EU Directive (2008/50/EC). To evaluate the risks of exposure to atmospheric aerosols and provide the necessary scientific support to elaborate abatement strategies for air quality improvement, quantitative data of fine PM composition over long time-series are necessary (Mantas et al, 2014).

The Greater Athens Area (GAA), a region of 450 km^2 where half of the population of the country is accumulated (>4 million), is characterized by enhanced concentrations of locally emitted (Kanakidou et al., 2011) and long range transported particulate matter (Koulouri et al., 2008; Perrone et al., 2013; Remoundaki et al., 2013b), absence of precipitation from spring to late autumn, favorable conditions for the formation of photochemical smog and unfavorable topography for dispersion of air pollutants. On a yearly basis the northern sector, which covers Central and Eastern Europe as well as part of the Western Turkey, is the most important, accounting for almost two thirds of the air masses arriving at GAA. Southern winds, responsible for the transport of Saharan dust during dust events, are very frequent during spring and autumn, contributing up to 25% of the prevailing air masses (Papadopoulou et al., 2009).

Results from systematic monitoring of PM_{10} concentrations and composition determinations are the most frequent in literature for Greek urban environments and have shown that the EU limit of 50 μg/m^3 is very often exceeded (Grivas et al, 2008; Terzi et al, 2010; Theodosi et al, 2011). Results on $PM_{2.5}$ concentration levels and composition are few and recent and have also shown frequent exceedances of the annual target value of 25 μg/m^3 (Theodosi et al., 2011).

The purpose of this paper is the experimental study of physicochemical characteristics of $PM_{2.5}$ and the comparison to those of PM_{10}. To clarify their role in health and the climate, not only the determination of their concentrations is required (requested by legislation) but the determination of their composition is also necessary. A description of the experimental sampling procedure and the methods of determination of the physicochemical characteristics of $PM_{2.5}$ and PM_{10} will be presented. Specifically it will be presented the method of determining the daily concentrations of ion fraction and the methodology of observation of samples in a scanning electron microscope (Scanning Electron Microscope) while chemical microanalysis (EDX) is simultaneously performed.

An effort is done to correlate the composition of $PM_{2.5}$ and PM_{10} to their origin. For this purpose, a series of 10 $PM_{2.5}$ and 10 PM_{10} daily samples were collected (20 samples total), from May to June 2014 at the National Technical University of Athens Campus. In the present work, the comparison of concentrations and composition between $PM_{2.5}$ and PM_{10} are performed. Water soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) were determined. The composition of PM, is examined and discussed in terms of ion concentrations levels and their relative contribution to the PM mass. For the ion fraction, the ion balance is presented. Moreover, concentration maxima of Ca^{2+} and SO_4^{2-} were associated to the air masses origin using wind roses and back trajectories. Finally,SEM-EDS analysis provided supplementary information on the morphology, composition and origin of the PM.

II. Methodology

A. General

The figure below (Figure 1) illustrates briefly the methodology used in this work, the stages followed to

determine the concentration, composition and morphological characteristics of $PM_{2.5}$ and PM_{10}.

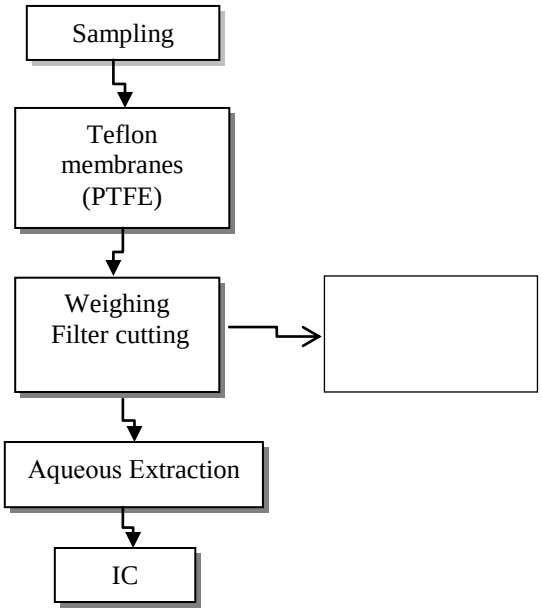

Figure 1. Methodology followed in this thesis

B. PM Sampling and Concentrations Determinations

Aerosol samples were collected at the top of the building of the School of Mining and Metallurgical Engineering at the National Technical University of Athens campus at 14 m above ground level. Twenty samples ($10PM_{2.5}$ + $10PM_{10}$) have been collected from 21 May to 7 June 2014. The sampling point is fully exposed to wind and free all-around of other obstacles (Remoundaki et al., 2011). PM sampling was carried out using two TCR TECORA (Sentinel PM) operating at 38.33 L/min, constructed and calibrated in order to comply with European Standards EN14907, EN12341 for standard sampling of $PM_{2.5}$ and PM_{10} respectively. The sampling device operates with autonomy of 16 samples loaded in a sequential cassette holder by programming the sampling span and duration. Aerosol samples were collected on PTFE membranes of 46.2 mm total diameter and 2μm pore size supported by ring suitable for PM sampling. The samplers were run in parallel, time-programmed to operate for five (A: 11:30-16:30) or three (B: 22:00-01:00) hours in the same place. The first sampled the $PM_{2.5}$ fraction and the second the PM_{10} fraction.

Sampling material and filter keeping petri-dishes were pretreated by soaking in dilute nitric acid solution and thorough rinsing by ultra-pure water (18 Mfl/cm) and dried under the laminar flow hood of the laboratory. In order to determine PM concentrations, the membranes were weighted before and after sampling according to the procedure described in EN12341 (Annex C) using a Mettler Toledo MS105 with a resolution of 10 μg in the air conditioned weighing room of the laboratory.

The pre weighted membranes were loaded to the filter supports and sampler cassette under the laminar flow hood. Filter blanks and blank field samples were also prepared and analyzed together with samples.

C. Ion Chromatography

The concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+} were determined by ion chromatography (IC). Ions were determined by a Metrohm 732 IC Separation Center connected to a 732 IC conductivity detector and 753 Suppressor Module for anions determination. A Metrosep Anion Dual 2 column was used for anions determinations (eluent: 2 mmol/L $NaHCO_3$ - 1.3 mmol/L Na_2CO_3 with chemical suppression, flow: 0.8 mL/min) and a Metrosep C4150/4.0 was used for cations determinations (eluent: 1.7 mmol/L HNO_3, 0.7 mmol/L dipicolinic acid, Flow: 0.9 mL/min). The calculated detection limits were: Cl^-: 18 μg/L, NO_3^-: 2.7 μg/L, SO_4^{2-}: 14 μg/L, Na^+: 20 μg/L, K^+: 20 μg/L, NH_4^+ 20 μg/L, Ca^{2+}: 66 μg/L, Mg^{2+}: 20 μg/L (Remoundaki et al., 2013a).

D. Air Mass Trajectories and Local Meteorological Data

Four days air mass backward trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT-4) to gather information about the origin of the observed aerosols and the synoptic patterns corresponding to the period under study. The calculations were made for the arrival heights of 750, 1000, 1500, 2000, 3000 and 4000 m a.s.l. over Athens, Greece (NTUA site).
Wind roses have also been calculated using the local meteorological data from the ground meteorological station of NTUA.

E. SEM-EDX analysis

Six filters have been selected for SEM-EDX analysis on three different dates, corresponding to Ca^{2+} concentrations maxima (Sahara origin) observed on 23/5/2014 and 29/5/2014 and high ion concentration levels of anthropogenic origin as NH_4^+ and SO_4^{2-} observed on 6/6/2014 (3x2 samples: $3PM_{2.5}$, $3PM_{10}$). The samples have been analyzed by Scanning Electron Microscope-Energy Dispersive X-Ray Spectrometry (SEM-EDX-JEOL JSM-840, Link 10000 AN), operating at an accelerating potential of 20 kV, probe current 3 nA and analysis time of 60 s. SEM images have been taken and many EDX spectra have been obtained on spots of the selected samples.

III. **SELECTED RESULTS**

In this section, selected results of the study are provided. Figure 2 illustrates the temporal variability in average atmospheric concentrations, daily concentrations of ion species of $PM_{2.5}$ and PM_{10} and mass closure of $PM_{2.5}$. Figure 3 illustrates distribution between the two PM fractions of water soluble ions, mean relative contribution of the main inorganic ion species of $PM_{2.5}$ and ion balance of PM_{10}. Figure 4 illustrates wind roses and back trajectories on 23/05/2014 and figures 5, 6 illustrate

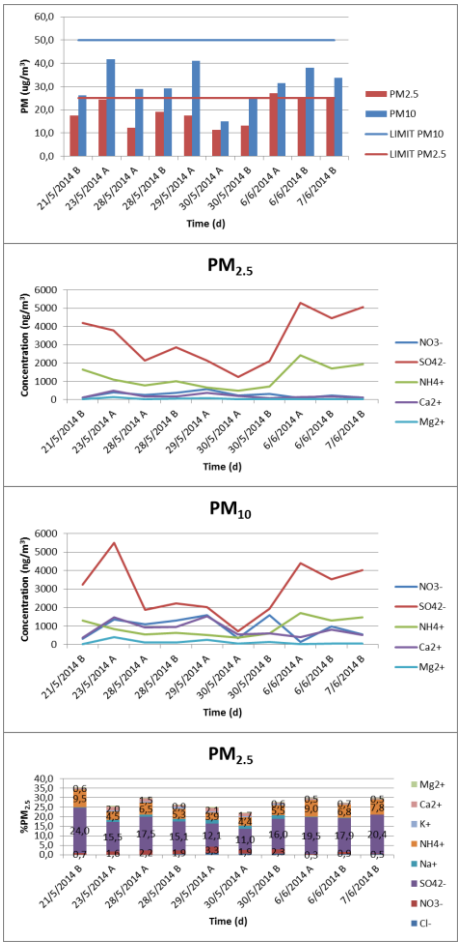

Figure 2. Temporal variability in daily atmospheric concentrations of $PM_{2.5}$, PM_{10}, temporal variability in daily concentrations of ion species of $PM_{2.5}$ and PM_{10} and temporal variability in mass closure of $PM_{2.5}$

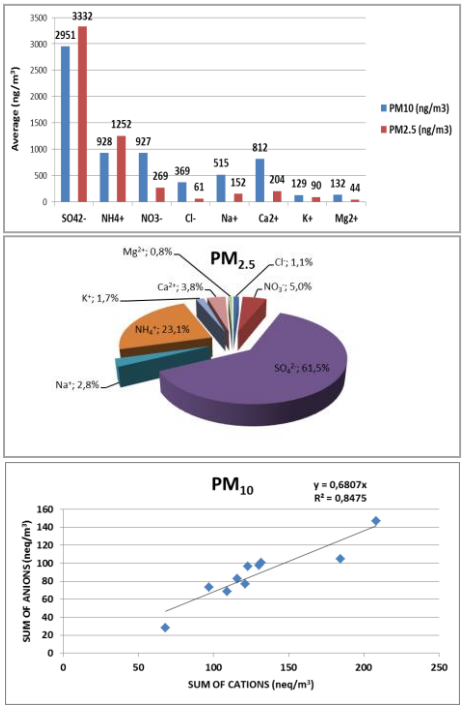

Figure 3. Distribution between the two fractions of water soluble ions, mean relative contribution of the main inorganic ion species of $PM_{2.5}$ and ion balance of $PM_{2.5}$.

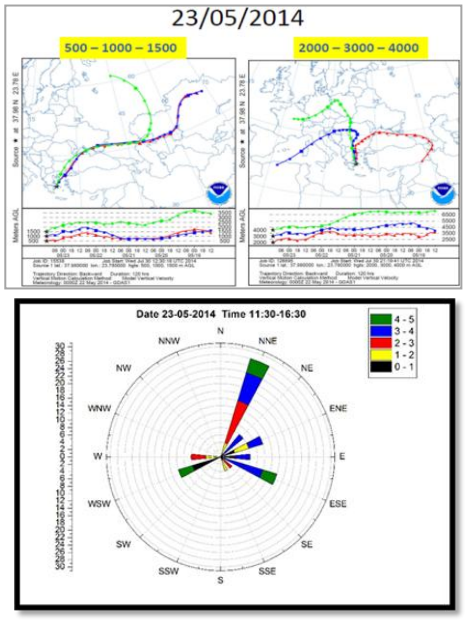

Figure 4. Back trajectories, Wind roses 23/5/2014

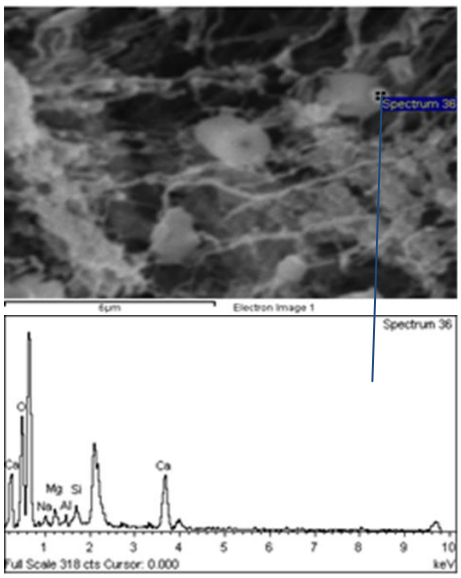

Figure 5. SEM – EDX, PP1 ($PM_{2.5}$), 23/5/2014

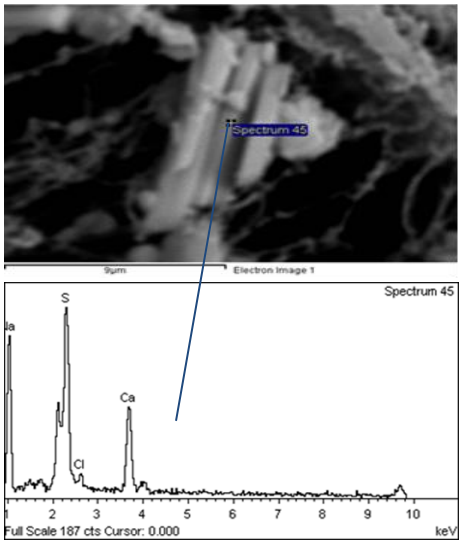

Figure 6. SEM – EDX, PP3 (PM_{10}), 23/5/2014

SEM-EDX analysis on 2 selected samples ($1PM_{2.5}$ + $1PM_{10}$) on the same date.

The average atmospheric concentrations of $PM_{2.5}$ and PM_{10} are 18 and 31 $\mu g/m^3$ respectively. The legal limit of 25 $\mu g/m^3$ of $PM_{2.5}$ is exceeded only in one sample on 6/6/2014 while simultaneous maximum for SO_4^{-2} was observed. There is no exceedance of 50 $\mu g/m^3$ limit concerning PM_{10} but in two cases (23/5/2014, 29/05/2014) the average atmospheric concentration exceeded the value 40 $\mu g/m^3$. Simultaneous maxima for both PM_{10} and SO_4^{-2} were observed on 23/5/2014 (see figure 2).

The ion concentration levels revealed that PM main mass is attributed to SIA (89.6% and 70.8% for $PM_{2.5}$ and PM_{10} respectively) with SO_4^{-2} the main component (61.5% and 43.5% for $PM_{2.5}$ and PM_{10} respectively). Ca^{2+}, Mg^{2+}, Na^+, Cl^- concentration levels are increased in coarse fraction (PM_{10}) due to their origin: crustal and marine (see figure 3).

Ion imbalance is attributed to CO_3^{2-} anions deficiency associated with Ca^{2+} which were not determined, especially for PM_{10} fraction (see figure 3).

SIA (Secondary Inorganic Aerosol) contribution to $PM_{2.5}$ and PM_{10} mass closure is 25% (28% ion species total) and 16% (22% ion species total) respectively (see figure 2).

On 23/5 where Ca^{2+} and SO_4^{2-} concentrations show sharp increases, the prevailing winds are north-northeast while the day before south-southwest winds are prevailing and air masses are coming from Central, Eastern Europe and from East Turkey and North West Africa at different heights. So the particles in this case have mixed origin with natural and anthropogenic component and increased concentrations of both Ca^{2+} and SO_4^{2-} ions (see figure 4). On 29/5 a clear Saharan dust transport episode was registered while on 6 June north winds transport fine particulates of anthropogenic origin rich in SIA.

Scanning Electron Microscopy observation coupled with Energy Dispersive X-ray analysis (SEM-EDX) results gave important information about the sizes, the morphology and the composition of PM. On 23/5 samples (1 sample $PM_{2.5}$, 1 sample PM_{10}), particle agglomerates were abundant in $PM_{2.5}$ fraction, most of them having sizes <2.5 μm while on coarse fraction having sizes >2.5 μm due to their nature and condition of formation as well as the distance from their source of origin. Dust particles were characterized by a high content in aluminosilicates (clays). Dust particles were very rich in calcium which is distributed between Ca-Si (smectite) and gypsum particles. Particles containing smectite have been detected by SEM-EDX analysis several times while quartz, illite and kaolinite have been also detected. Particles containing sulfates as gypsum, $MgSO_4$ and Na_2SO_4 have been detected by SEM-EDX analysis several times on PM_{10} sample while sea salt particles have been also detected (see figures 5, 6).

IV. CONCLUSIONS

Despite the short sampling time the results are in accordance with the literature and significantly influenced by dust transport events of desert areas of Africa.

SEM-EDX results on 23/5 confirm the elemental composition results from literature and are consistent with the origin of the dust particles from Western Sahara and Northern Algeria. Heavy metals and sulfur localization was extremely difficult in $PM_{2.5}$ possibly due to the fact that these elements were associated with ultra-fine particles of sub-micron sizes while in PM_{10} case the formation of sulphates of larger sizes was favored.

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