

## ATLAS OF AIRBORNE PARTICLES FROM KOZANI AREA, NORTHERN GREECE

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### Abstract

During a whole year (March 2003 to February 2004), several filters that capture airborne particles were collected from seven sampling sites spread throughout the Ptolemais-Kozani region (Western Macedonia), northern Greece. Environmental Scanning Electron Microscopy (ESEM), coupled with Energy Dispersive X-Ray analysis (EDX) was employed for the characterisation of the airborne particles. A classification of these airborne particles is attempted in this study. Aerosols with various morphological characteristics (angular, irregular, rounded, spherical, spheroidal, acicular), variable size (mostly between 5µm and 20µm) and composition (aluminosilicates, oxides, carbonates, sulphates, metallic) were recognized. The airborne particulates were also categorized according to their origin. Geogenic, biogenic, anthropogenic (mainly fly ash released from lignite-fired power plants), carbonaceous and metalliferous (mainly iron and copper enriched) were the main categories. A database of characteristic airborne particles from Kozani area is being created using a simple software package, in order to help similar studies in the future.

**Key words:** SEM/EDX, air pollution, source identification, geogenic, anthropogenic.

### Περίληψη

Κατά την διάρκεια ενός ημερολογιακού έτους (Μάρτιος 2004-Φεβρουάριος 2004), αρκετά φίλτρα συλλογής αιωρούμενων σωματιδίων λήφθηκαν από επτά θέσεις δειγματοληψίας στην γεωλογική λεκάνη Αμυνταίου-Πτολεμαΐδας-Κοζάνης. Πραγματοποιήθηκε ανάλυση των αιωρούμενων σωματιδίων με χρήση του «Περιβαλλοντικού» Ηλεκτρονικού Μικροσκοπίου (ESEM). Ταυτόχρονα, προσδιορίστηκε η χημική σύσταση των σωματιδίων με χρήση του συστήματος διασποράς ενέργειας (EDX). Τα σωματίδια ταξινομήθηκαν σε διάφορες κατηγορίες με βάση την προέλευσή τους (ανθρωπογενή, γεωγενή, βιογενή), το μέγεθός τους (μέση διάμετρος 5-20 µm), τη μορφολογία τους (γωνιώδη, ασύμμετρα, σφαιρικά, επιμήκη) και τη σύστασή τους (αργιλοπυριτικά, ανθρακικά, οξειδία, θειϊκά, μεταλλικά, ανθρακούχα). Δόθηκε έμφαση σε σωματίδια ιπτάμενης τέφρας που προέρχεται από την καύση των λιγνιτών στους θερμοηλεκτρικούς σταθμούς της περιοχής. Δημιουργήθηκε μία βάση δεδομένων με χαρακτηριστικά αιωρούμενα σωματίδια (όπως αυτά

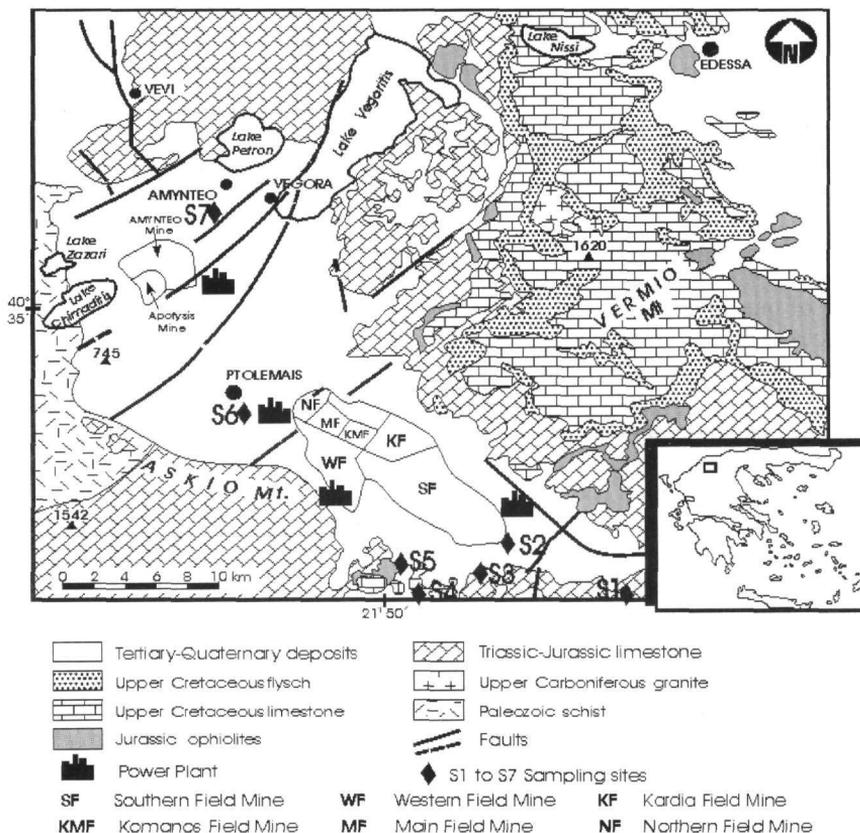
προσδιορίστηκαν στην παρούσα μελέτη), με σκοπό να βοηθήσει παρόμοιες μελλοντικές έρευνες στην περιοχή.

Λέξεις κλειδιά: SEM/EDX, προέλευση, ανθρωπογενή, γεωγενή, βιογενή.

## 1. Introduction

The connection between exposure to airborne particles and its adverse effects on human health have been well investigated (Breed *et al.* 2002). It is therefore crucial to understand the nature of the particulate matter, especially in areas which suffer from heavy air pollution problems (e.g. industrial territories or urban regions). This could be helpful for the local and national authorities or environmental organisations, in order to assess the environmental impacts of human activities and schedule plans to enhance ecological protection and corroborate with the air pollution problems.

The source identification of aerosols is often based on their morphological, mineralogical and chemical characteristics. For this reason, several multidisciplinary analytical methodologies have been applied, such as X-Ray Fluorescence (XRF), Inductively Coupled Plasma spectroscopy (ICP), Neutron Activation Analysis (NAA), Electron Microprobe (EMPA), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) etc. (Paoletti *et al.* 2002, Ebert *et al.* 2004, Kupiainen and Tervahattu 2004, Goforth and Christoforou 2006, Suzuki 2006).



**Figure 1 - Simplified geological map of the Ptolemais-Kozani area, showing the seven sampling sites (S1 to S7), the opencast lignite mines and the lignite-fired power-plants**

In the Western Macedonia region of northern Greece, heavy air pollution problems have been demonstrated, attributed mainly to the extensive lignite mining and burning for energy production. The investigation of this problem incorporated statistical evaluation of TSP, PM10 and PM2.5

concentrations, chemical mass balance source apportionment studies and creation of mathematical models based on the meteorological and topographical data (Triantafyllou *et al* 2002, Samara 2005, Zoras *et al.* 2006). The present study employs the Environmental Scanning Electron Microscopy (ESEM) technique for the identification of individual airborne particles. Environmental Scanning Electron Microscopy (ESEM) is a special type of scanning electron microscope that works under controlled environmental conditions and does not require a conductive coating on the specimen, thus providing fast results. ESEM, coupled with energy dispersive X-ray analysis (EDX), provides information on individual airborne-particle analysis and reveals definitive information about elemental associations, agglomerations and variation of composition with particle size. A classification of the airborne particles is being attempted, based on their origin and morphological and compositional characteristics.

## 2. Sampling area

The Florina-Ptolemais-Kozani basin (sampling area) is situated within Western Macedonian region (Fig. 1). This basin is 50 km long and 10–25 km wide, relatively flat-bottomed at about 650m above sea level, surrounded by high mountains. Climate is continental Mediterranean characterized by low temperatures during winter and high temperatures during summer. Prevailing winds are weak blowing mostly along the NW/SE axis of the basin (Samara 2005).

Most of the greek lignite deposits are located in this large, intensively exploited area. This area is exploited by opencast mining and feeds nearby lignite-fired power stations. Five thermal power stations are located in this basin which account for 80 % of the total lignite burning electricity production in Greece. About 64 Mt of lignite, produced by open-cast mining in four mines, are annually used in the power plants leading to an annual fly ash production of nearly 13 Mt (Kantiranis *et al.* 2006). The area has suffered in the past from high ambient levels of total suspended particles (TSP), although electrostatic filters were used in the power plants.

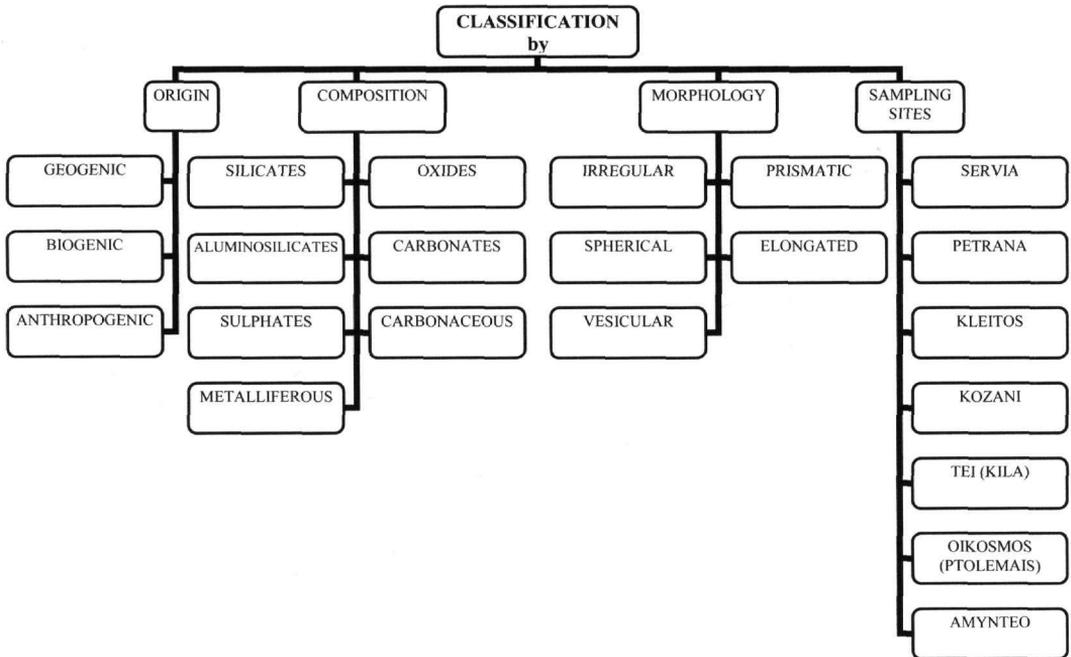
## 3. Materials and Methods

Over a period of one year (March 2003 to February 2004), data was collected by stationary and portable collectors, placed throughout the region, at seven sampling sites (Fig. 1). The sampling took place on ten randomly chosen dates, covering all seasons. Total suspended particles (TSP) were collected on fibre-glass and cellulose filters, while PM10 and PM2.5 (particulate matter with a diameter lower than 10 $\mu$ m and 2.5  $\mu$ m respectively) on teflon filters. Several square centimeters of filter paper were cut from the centre of each filter paper, and examined within the ESEM without any form of preparation (i.e. no gold or carbon coating). A Philips XL30 environmental scanning electron microscope (ESEM), equipped with a LaB<sub>6</sub> filament, was used to image and elementally analyse the filter samples of the present investigation. The ESEM was operated in low-vacuum mode, at a pressure of between 0.5 and 0.7 Torr, under a water vapour atmosphere. Other operational parameters were as follows: working distance 10mm, and operating voltage 20 kV. Imaging was predominantly carried out in backscattered electron mode (BSE). Elemental analysis was carried out by energy dispersive X-ray analysis (EDX), under the same operational parameters as for imaging. EDX analysis was carried out at each analysis point for 100 live seconds, and the elements present were both qualitatively and quantitatively measured. Approximately five hundred ESEM images and EDX spectra of individual airborne particles were obtained.

## 4. Results and Discussion

Based on the images and chemical analysis of the airborne particles, using the ESEM-EDX equipment, several categories were identified based on their provenance and their morphological and compositional characteristics. Another grouping was also created according to the sampling sites. All these data are being incorporated in a database of airborne particles from the Ptolemais-

Kozani region, which will be useful for similar studies of local and national authorities, as well as for other scholars working in the region. The aforementioned categorization is schematically demonstrated in Figure 2.

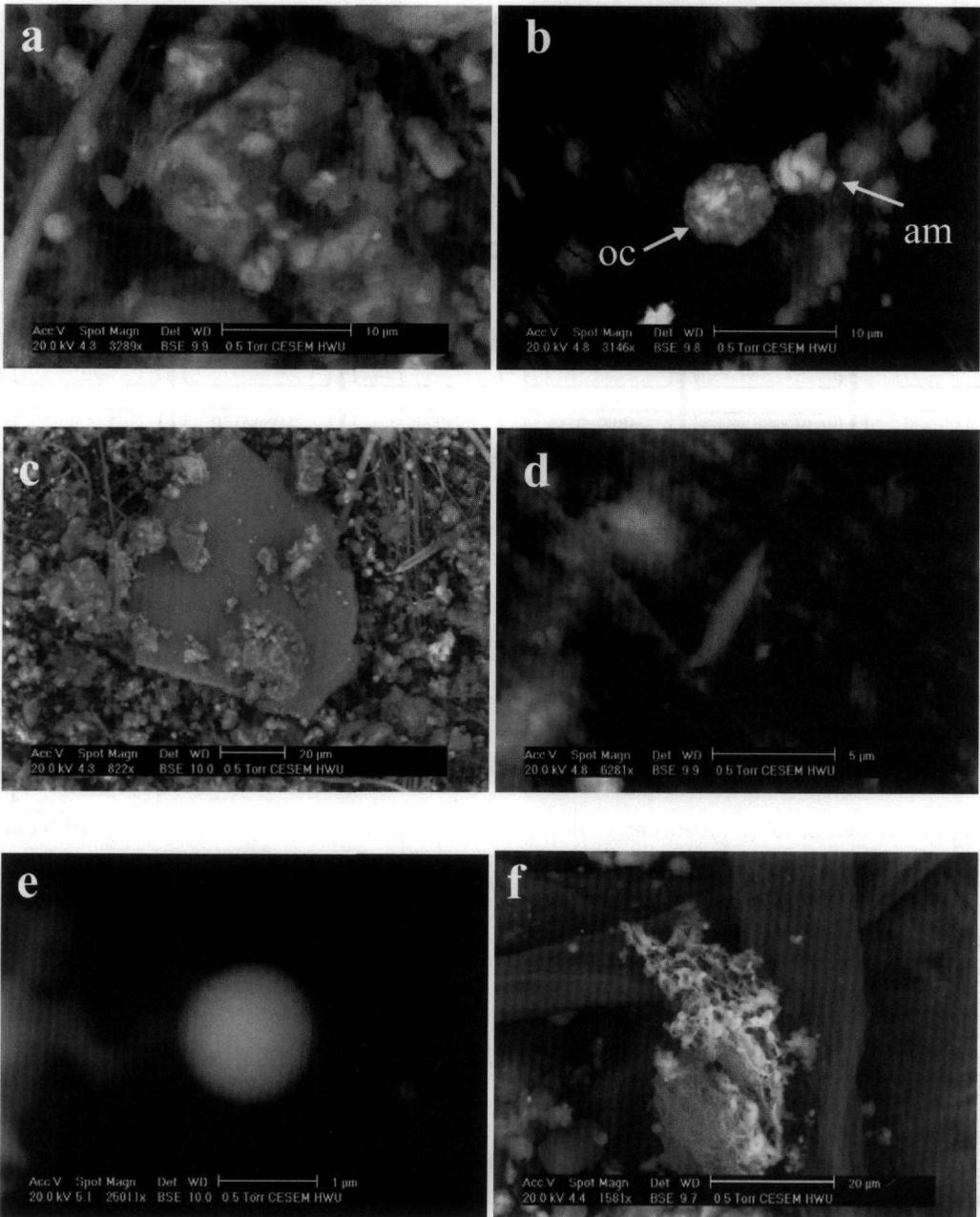


**Figure 2 - Schematical presentation of the categorization of airborne particles collected from Ptolemais-Kozani area, northern Greece.**

It should be noted however that the majority of the analysed airborne particles consist of aggregates of various composition with a minerogenic (natural) origin. Moreover, the agglomeration of smaller particles often hindered the identification of individual particles.

#### 4.1. Morphology and size of airborne particles

The size of the analysed individual airborne particles ranged between  $<1 \mu\text{m}$  and  $50 \mu\text{m}$ . The majority of the particulates captured in TSP filters had a size between  $5\mu\text{m}$  and  $20\mu\text{m}$ . PM10 and PM2.5 revealed obviously smaller sizes (fine and ultrafine dimensions). Nevertheless, there were observed a few large particles ( $>10 \mu\text{m}$  and  $>2.5 \mu\text{m}$ ) in the PM10 and PM2.5 filters respectively, a fact that suggests inadequate separation of the sampling equipment. According to their morphological characteristics, there were found particulates with an acicular (elongated), prismatic (platy, hexagonal, rhombic, cubic etc.), irregular, rounded, spherical or spheroidal shape, and a dense, porous or vesicular structure. Some of the above mentioned characteristic features are shown in Figure 3. A polygonal crystal, is shown in Figure 3a, a prismatic and an amorphous particle in Fig. 3b, a platy flake in Fig. 3c, a needle-like (acicular) crystal in Fig. 3d, a spherical particle in Fig. 3e and a porous particulate in Fig. 3f. Fine airborne particles with a diameter lower than  $10 \mu\text{m}$  are taken into special consideration, since these particles (PM10) are regarded as respirable and may cause damage to the respiratory system of humans. Only a few minute fibre particles were observed, a fact that is significant when thinking of the health impacts of ultrafine fibrous aerosols. Nevertheless, the chemical composition of such particles (e.g. soluble transition metals like iron, titanium or zinc in our study), their acidity and ultrafine size could pose a threat to human health. The latter aspect is discussed below.



**Figure 3 - Classification of airborne particles according to their morphology: a) a polygonal prismatic crystal, b) an octagonal euhedral crystal (*oc*) and an irregular amorphous particle (*am*), c) a platy crystal, d) an acicular, needle-like particle, e) a fine spherical particle, f) a porous (vesicular) aggregate**

#### **4.2. Origin and composition of airborne particles**

The airborne particles of our study could be classified according to their origin (provenance) and composition to the following dominant groups: *geogenic* particles (mineral fragments, aggregates and agglomerates of various composition derived from soils and weathered rock surfaces); *biogenic* aerosols (organic plant material, fungal hyphae and spores); *fly ash* airborne particles (fly

ash of various morphology and composition, coming from the nearby power plants); *metalliferous* (*anthropogenic*) particles.

#### 4.2.1. Geogenic particles

Geogenic are mineral particulate aerosols derived from soils, sediments and weathered rock surfaces. The release of natural aerosols due to extensive mining activities in the area contribute greatly to the geogenic airborne particles found in this study. Yet, it is very difficult to distinguish between natural aerosol dust and dust derived from the mine outcrops or transportation of sterile rocks from opencast lignite mines. Some characteristic natural particles are shown in Figure 4. In particular: a rhombohedral calcite crystal ( $\text{CaCO}_3$ ) in Fig. 4a and an elongated quartz crystal ( $\text{SiO}_2$ ) in Fig. 4b. Several other common geogenic particles were also identified, such as feldspars (Fig. 5a), phyllosilicate minerals (e.g. clays and micas of Fig. 5b), carbonates (Fig. 5c), oxide-hydroxides (Fig. 5d) etc., along with some uncommon minerals of probably natural origin (e.g. zircon, titanite, apatite). Fine sulphate particles were also rather abundant. Such sulphates could be regarded as a sampling artifact, originating from the reaction of gaseous pollutants ( $\text{SO}_2$ ) with the Ca-rich dust particles already collected in the filter. The pathological effects of prolonged exposure to natural aerosol dust have been demonstrated (Derbyshire 2005). Besides, some of the identified minerals are known for health implications. For example, quartz could cause silicosis; clay minerals refer to kaolinosis; and iron carbonate/oxide is connected to siderosis (Jones *et al.* 2006).

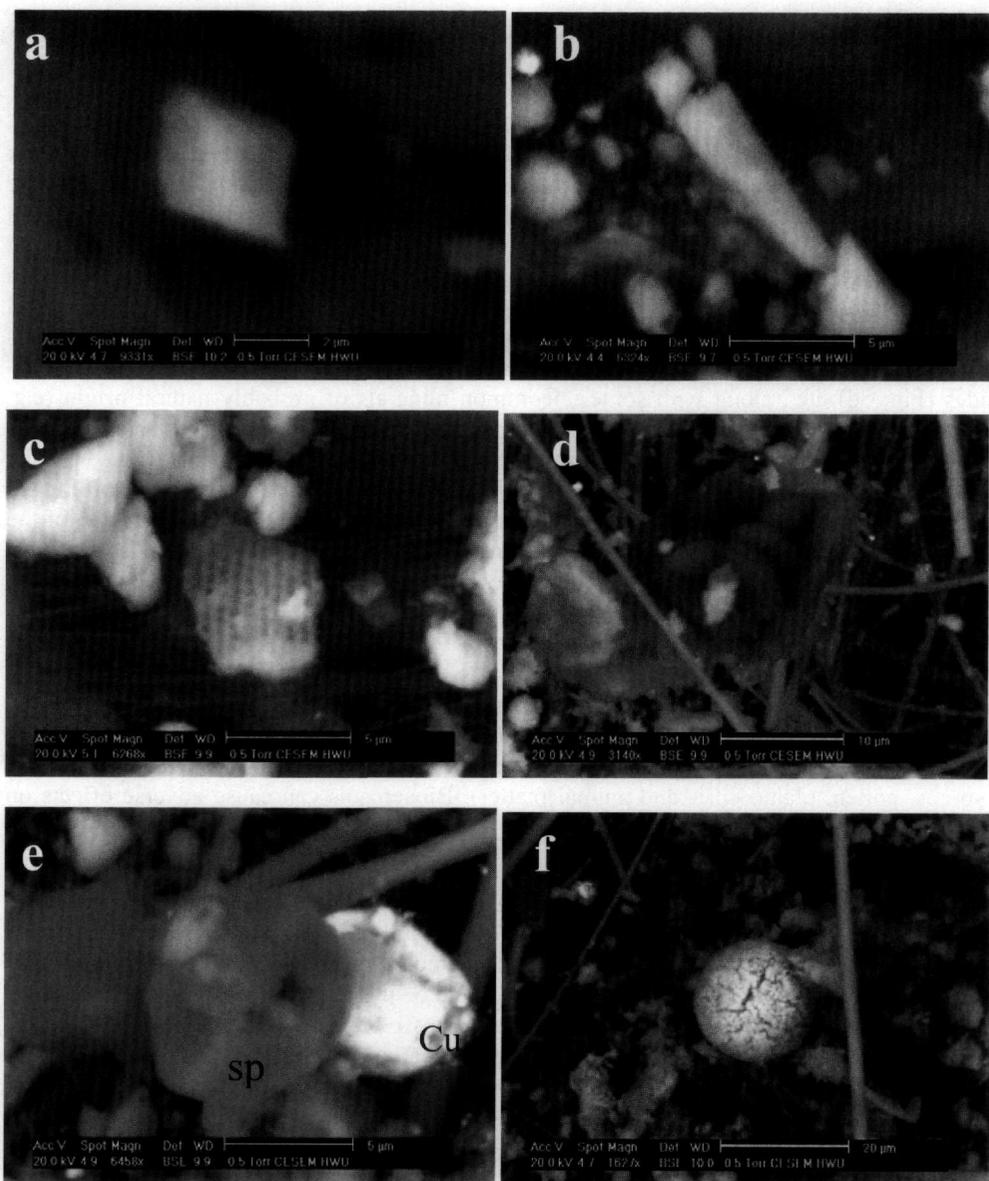
#### 4.2.2. Bioaerosols

Biogenic airborne particles, the so-called bioaerosols, have also been observed in our study. Bioaerosols are known as a wide spectrum of dead or alive airborne particles of biological origin, including microorganisms and fragments of all varieties of living matter (i.e. viruses, bacteria, fungal spores, pollen, plant debris and animal matter). Bioaerosols can cause adverse effects on humans, animals and plants (Ryves *et al.* 2003).

In our study, fragments of valves and frustules of circular, elliptic and square diatoms were recognised, all of terrestrial origin, belonging to Centrophycae and Pennatophyceae classes and Aulacoseira and Fragilaria genus. A fragment of diatom frustules belonging to Centrophycae class is shown in Fig. 4c. The identified diatoms are considered as recent ones, derived from surface soils and sediments. Two other less possible sources could be the following: they might have come during strong air movements (episodes) from the outcrops of the opencast lignite mines or the dumping areas of the overburden rocks, where Neogene, diatom-rich sediments are exposed to air (Ognjanova-Rumenova 2003), or they might be present in the lignite, feeding the power plant and due to their composition (biogenic silica) and small size might be released to the atmosphere as fly ash particles. A bunch of fungal spores is shown in Fig. 4d. It is well known that human exposure to airborne fungal spores might cause adverse health effects, especially respiratory symptoms (Liao *et al.* 2004). Fungal spores were more abundant during late spring-early summer period, while diatoms were observed throughout the year. A spore and/or pollen airborne particle of unknown origin is also shown in Fig. 4e.

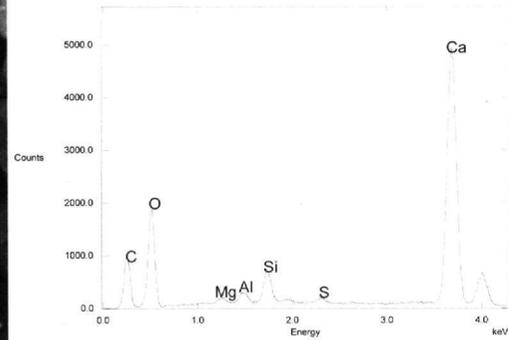
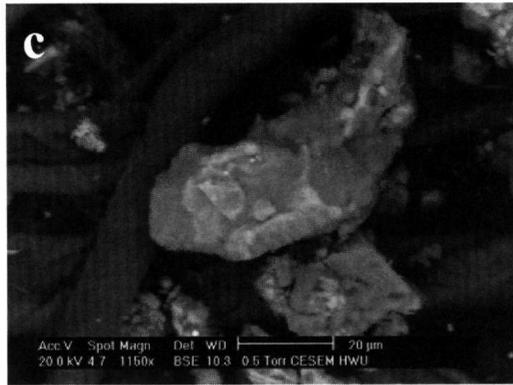
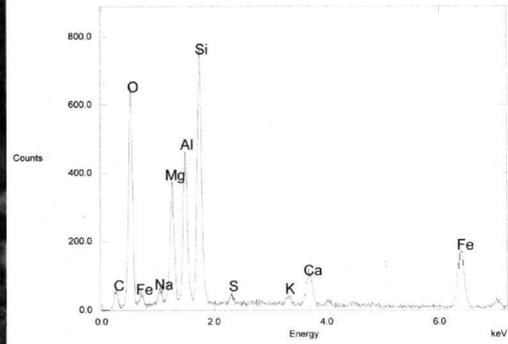
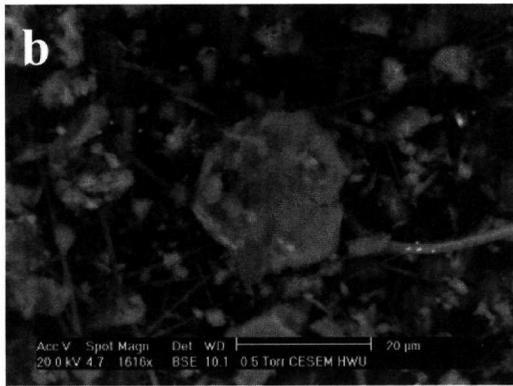
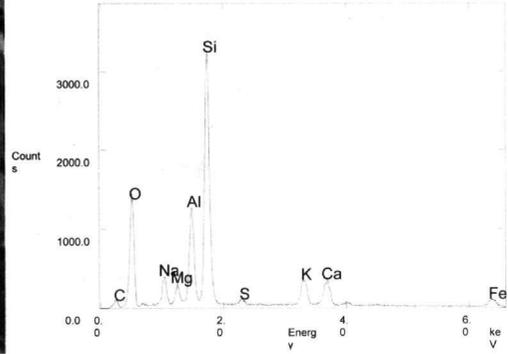
#### 4.2.3. Fly ash particles

Fly ash particles consist of inorganic amorphous and crystalline constituents. Emphasis was given on the amorphous particles, since it is very difficult to distinguish between geogenic and anthropogenic crystalline particles. Considering that no other heavy industrial activities (e.g. refineries, steel production, blast furnaces, large-scale cement industries) exist in the area, that could produce such airborne pollutants, these amorphous, spherical, inorganic particles are most likely related to fly ash (Lee *et al.* 2004). The amorphous components consist mostly of spheres and spheroids, although angular and irregular particles are not absent. Characteristic iron-rich plerospheres (i.e. cenospheres that capsulate other smaller pre-existing aggregates, particles and agglomerates) are shown in Fig. 4f and Fig. 5d. The chemical composition of the fly ash-airborne

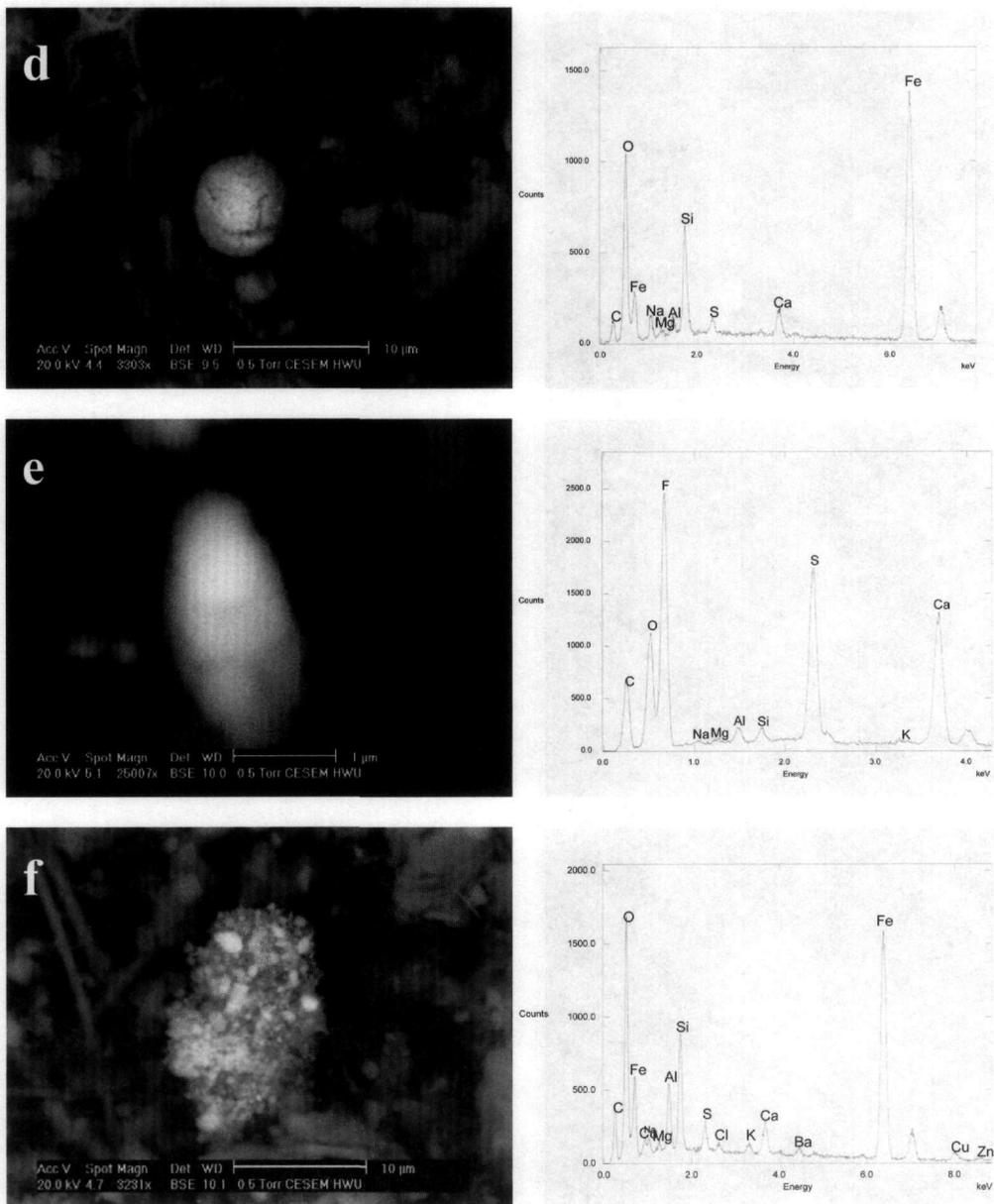


**Figure 4 - Classification of airborne particles according to their origin: a) a geogenic rhombohedral calcite, b) an elongated quartz crystal, c) a fragment of diatom frustules belonging to Centrophycae class (biogenic), d) fungal spores (biogenic), e) a spore/pollen (biogenic) [*sp*] and a Cu-rich particle (anthropogenic) [*Cu*], f) a Fe-rich, fly ash plerosphere (anthropogenic)**

particles is mainly aluminosilicates and iron and/or calcium- rich particles. The presence of potential toxic metals (e.g. copper and zinc) in several fine fly ash particles is also evident. In addition, unburnt lignite (char) was observed, which originates from the incomplete combustion of lignite. Similar images of fly ash particles of the same region have been published previously (Georgakopoulos *et al.* 1992, Fernandez-Turiel *et al.* 2004, Iordanidis *et al.* 2005).



**Figure 5 - ESEM images and EDX spectra of airborne particles of different composition: a) a feldspar crystal  $[(K,Na,Ca)AlSi_3O_8]$ , b) a clay or mica flake, c) a calcium carbonate  $[CaCO_3]$ , calcite] particle**



**Figure 5 (continued) - ESEM images and EDX spectra of airborne particles of different composition: d) an iron oxide spherical particle, e) an ultrafine sulphate particle, f) an agglomeration of minute Fe-rich particles, with minor amounts of Cu and Zn metals**

The temporal and spatial distribution of fly ash-airborne particles did not show significant variation. Fly ash was found in all sampling sites (predominantly nearby power stations) and all sampling dates. Fine and ultrafine particles were recorded mainly in remote areas, where they have obviously been transported by the winds (sampling sites S1, S4 and S5). Larger fly ash particles are generally concentrated proximal to power stations (sampling sites S3 and S6).

Several studies have well demonstrated the environmental impacts of the lignite-induced air pollution in the Ptolemais-Kozani area (Stalikas *et al.* 1997, Kallithrakas-Kontos *et al.* 1998, Triantafyllou 2001, Samara 2005). A study of the detrimental effects on the respiratory system of

children residing in Western Macedonia, Greece, has showed a high prevalence of rhinitis and infectious bronchitis especially in the city of Ptolemais, and these findings were attributed to the heavy environmental pollution (Sichletidis *et al.* 2005).

#### 4.2.4. Metalliferous particles

The dominant metalliferous airborne particles are iron and copper-rich particles. A single fine copper-rich particle is shown in Figure 4e, and agglomeration of iron oxides, rich in trace metals (Zn, Cu) is shown in Fig. 5f. These particles are likely to be associated with motor vehicle activity, originating from brake and tyre wear (Cyrys *et al.* 2003, Arditoglou and Samara 2005, Lough *et al.* 2005). Furthermore, Fuge (2005) noted that motor vehicles could be a source of copper pollution, it being released from copper wiring, thrust bearings and brakes.

Of specific concern has been the potential threat posed by exposure to particles containing transition metals. Transition metal toxicity is considered to occur through an oxidative/free radical pathway leading to respiratory inflammation (Fernandez *et al.* 2002, Powell *et al.* 2002, Cassoni *et al.* 2004). The finest fraction of particulate matter deserves special attention for it carries deeply into the lung these adsorbed chemicals (Breed *et al.* 2002).

## 5. Conclusions

The concluding remarks of the present study are the following:

- ESEM coupled with EDS system helped us to assess qualitatively the contribution of airborne particles of various origin, morphology and composition to the air pollution of Kozani's region.
- The airborne particles were classified as geogenic, biogenic and anthropogenic (mainly fly ash). Quartz, calcite, feldspar, mica, and clays are some of the common minerogenic (natural) airborne particles observed in this study, while diatoms, spores/pollen and fungal spores are some of the biogenic airborne particles identified.
- Characteristic features of fly ash particles were also identified. Fine fly ash particles were found in remote areas, whereas the coarser ones were observed in the vicinity of the power plants. Metalliferous particles (mainly Fe and Cu-rich particles) were also observed, most likely having a vehicular (exhaust, tyre and brake abrasion) origin.
- A database is being created including ESEM images and EDX spectra of characteristic individual airborne particles from Ptolemais-Kozani area, which could be useful for similar studies in the future.

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