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Morphological characteristics of magnetic particles and their environmental impact: the case of Sarigiol basin (Greece)

Chrysoula Chrysakopoulou[1,*], *Dimitrios* Vogiatzis[1], *Alexandros* Drakoulis[1], *Lambrini* Papadopoulou[1], and *Nikolaos* Kantiranis[1]

[1]Department of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Abstract. Magnetic particles were separated from soil and sediment samples from the Sarigiol basin in northwestern Greece in order to study their morphological characteristics with scanning electron microscopy. They appear in the form of octahedrons and spheres and they have lithogenic and anthropogenic source, respectively. The source of the lithogenic magnetic particles is the ophiolite complexes at the NE and SW part of the basin while the fly ash and its dispersion from the two power plants located in the research area is the source of the anthropogenic magnetic particles. The surface structure of magnetic particles is either simple or more complex while the average size of the spheres is 10-50 μm. Highest values of the ratio of the anthropogenic to lithogenic magnetic particles at the NE and locally at the NW, N and SW part of the study area are a strong evidence of the environmental footprint that anthropogenic activities have at the upper soil horizons of the Sarigiol basin.

1 Introduction

Environmental pollution is probably the world's greatest problem facing humanity. Industrial and urban development have caused an adverse redistribution of metals in the environment and therefore in the soils. Magnetic particles are one of the best tracers of environmental pollution. Fly ash produced by fossil fuel combustion at high temperatures is probably the most common source of anthropogenic particles in the upper soil horizons [1], while iron or steel metallurgy and even vehicular traffic contribute significantly to their presence in topsoil in areas close to large urban and industrial centres.

Magnetic particles consist mainly of strongly ferromagnetic minerals such as magnetite and maghemite but also less strong such as hematite, siderite and wolframite. In soils that have not undergone any kind of anthropogenic activity, the presence of natural magnetite is mainly due to the presence of ultramafic/mafic rocks such us ophiolite complexes the clastic material originated from them, but also to the deposition of ferrous minerals from soil solutions.

Fly ash is a particularly complex material, with varied composition and heterogeneity. During coal combustion, a part of the fly ash produced has magnetic properties. Participation of magnetic fraction in fly ash varies from 2 to 20% w.t [2] and it consists mainly of ferromagnetic minerals such as magnetite and maghemite, but sometimes magnesioferrite is also present. Magnetic particles of fly ash often form aggregates with aluminosilicate/silica mineral phases. Their difference from lithogenic magnetic particles lies mostly in their morphology, as they are mainly spherical and with a diameter of a few tens to hundreds of micrometres. Additionally, the formation of magnetite during fossil fuel combustion lasts only a few seconds, so its physical properties differ from those of lithogenic magnetite, which formed during a long-lasting crystallization. Anthropogenic magnetite has greater porosity than the lithogenic one, as a result of a lower density, magnetic susceptibility and hardness [3].

The average size of the fly ash particles ranges from 1 to 150 μm [4]. According to studies, there are differences in the size of anthropogenic magnetic particles depending on their source with their size decreasing starting with steel industry, in steam power plants and finally in vehicle exhaust [5]. The morphology of spherical magnetic particles formed during fossil fuel combustion is either simple or more complex with dendritic or skeletal-like structures. External factors such as the rate of temperature growth and supersaturation contribute significantly to the final morphological structure of the magnetic particles [3].

Northwestern Greece hosts the country's largest lignite centre, with its exploitation and combustion environmentally affecting the area of Kozani/Ptolemaida/Florina for decades. Fly ash particles produced by the steam-generated power plants of the lignite centre but also by its activities, are the main environmental pollutants of the area. The aim of the present study is the morphological characterization of magnetic particles from soil and sediment samples from Sarigiol basin (Kozani) and the mapping of the ratio anthropogenic to lithogenic magnetic particles in order to depict the extent of the pollution in the upper soil/sediment horizons. Magnetic particles were separated from soil and sediment samples and they were

* Corresponding author: chrysako@geo.auth.gr

morphologically observed by scanning electron microscopy (SEM). Appropriate software was used to map the spatial distribution of the ratio of the anthropogenic to lithogenic magnetic particles and then the corresponding map was created.

2 Methodology

The Sarigiol basin is located in Northern Greece and is the southern part of the Ptolemais basin. Around the perimeter of the basin, limestone formations have a strong presence while at the NE and SW part of the area there are occurrences of ultramafic rocks such us ophiolite complexes. The centre of the research area consists of Quaternary formations such as sands, talus/brecciated cones and clay formations.

The sampling was carried out in Sarigiol basin from 59 different locations. In total, 47 samples of surface sediment (0-10 cm) and 12 samples of soil from the weathering mantle above the bedrock, were collected. For the separation of the magnetic fraction, 20g of representative material (<2 mm) was disaggregated slightly in an agate mortar by hand. Then, this material was mixed with 250mL of deionized water, 10mL of dispersing agent [$(NaPO_3)_6$, 50g/L] and they were placed with a magnet in a beaker in order to extract the strongly magnetic particles, using a magnetic stirrer at low speed and without heat in order to achieve particle dispersion. The separation was repeated three times, after a period of 5, 2, and 1 min [6]. Magnetic particles extracted from each sample were dried at 110 ºC to constant weight and then weighed and placed in plastic vials for their morphological study using the Scanning Electron Microscope of the Laboratory of Electron Microscopy of Aristotle University of Thessaloniki. A representative amount of the magnetic fraction of each studied sample was placed on aluminium double-sided tapes and then on special samplers while before the observation they were coated with carbon. The studied samples were observed at randomly selected optic fields. For the mapping of the ratio of the anthropogenic to lithogenic magnetic particles, Surfer was used to create a grid with the spatial interpolation kriging method and later, in order to create the map, it was imported into QGIS 3.16.15. The extracted map was presented through a scaled colour gradation of filled contours based on the ranges of the ratio of the anthropogenic to lithogenic magnetic particles of each sample.

3 Results and discussion

Based on the morphological characterization of the studied magnetic particles, they appear in the form of octahedrons and spheres (Fig.1). The source of the octahedrons (pyramids-like) is the ultramafic rocks of the study area and specifically the ophiolite complexes and the NE and SW part of the basin (Fig.2). They are euhedral and their size ranges from 10 to 400μm. Their surface structure is characterized mainly as smooth (Fig.3), some particles are fragmented with their vertices being broken (Fig.4a), while a few of them have irregular surfaces (Fig.4b).

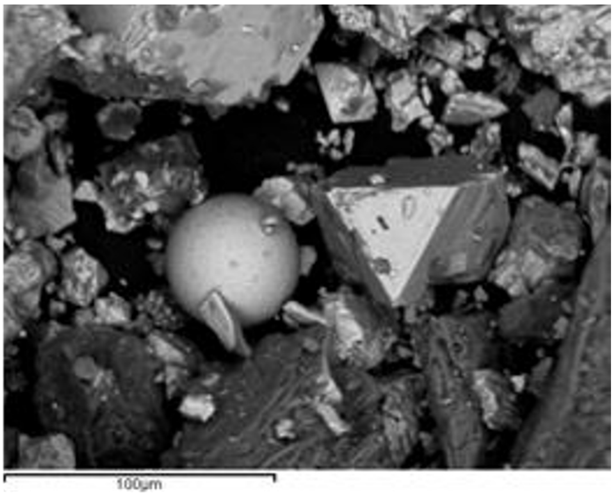


Fig.1. Magnetic particles in the form of octahedron (right) and sphere (left) from the studied samples of Sarigiol basin.

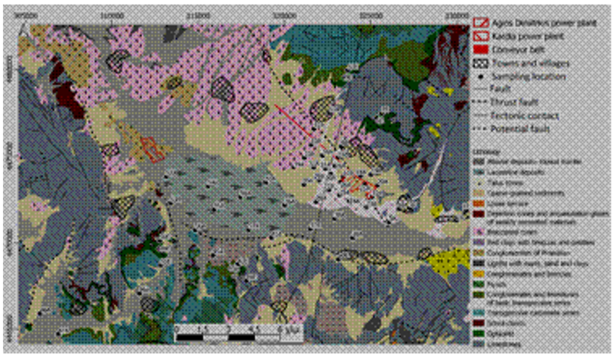


Fig. 2. Geological map of the study area (modified by EAGME).

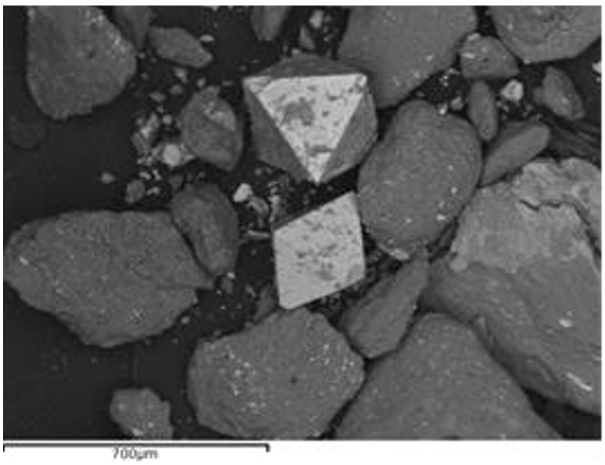
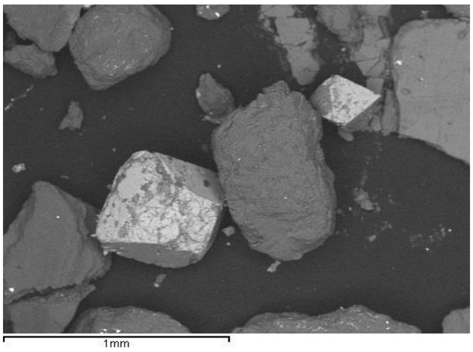
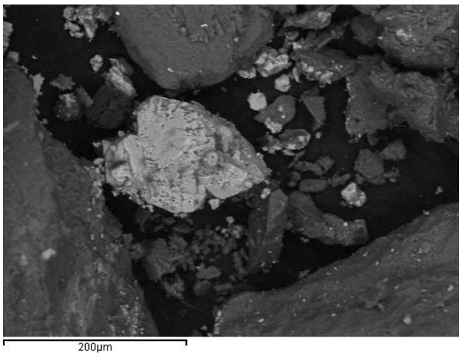


Fig. 3. Lithogenic magnetic particles in the form of octahedrons and with smooth surfaces from the studied samples of Sarigiol basin.



(a)



(b)

Fig.4a,b. (a) Fragmented lithogenic magnetic particle in the form of octahedron with a broken vertice and **(b)** lithogenic magnetic particle with irregular surface from the studied samples of Sarigiol basin.

The source, to which the presence of the magnetic spheres is attributed, is the fly ash produced by the activity of two electric power stations located in the study area, Agios Dimitrios and Kardia at the E and NW part of the basin, respectively. Their size ranges from 4.7 to 140 μm while the majority of spheres are between 10-50 μm (Fig.5). There are certain factors controlling the size of the fly ash particles. The composition of the initial coal seems to be the most important factor of all, while the distance from the power station, the height of the chimney and the combustion temperature contribute significantly to the fly ash particles size [7].

The surface structure of the spheres is either simple like smooth type (Fig.6) or more complex, as they are presented with crystalline-like patterns. Orange-peel (Fig.7a), thread-type (Fig.7b), blocky-style (Fig.8a) and spongy-type (Fig.8b) structures are very common while a limited number of them have lost their sphericity (Fig.8c) or have the form of aggregates (Fig.8d). The loss of sphericity or the formation of aggregates could be attributed probably to heterogeneous reactions of condensations during their transportations [8]. These more complex types of morphologies are very common in fly ash particles originating from coal combustion at very high temperatures [9].

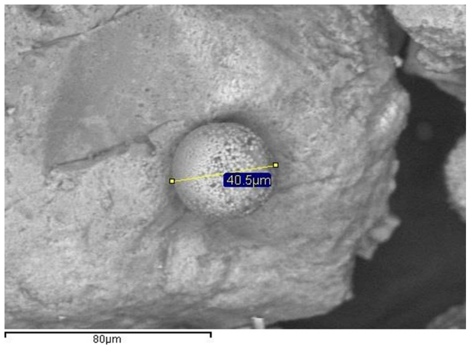


Fig.5 Anthropogenic magnetic particle in the form of sphere from the studied samples of Sarigiol basin.

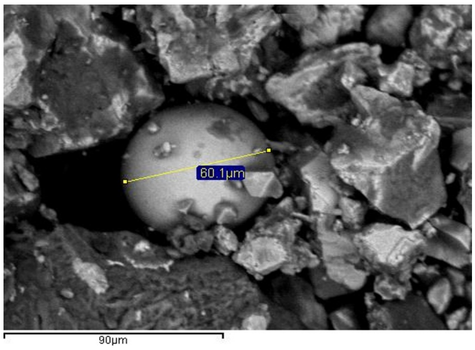
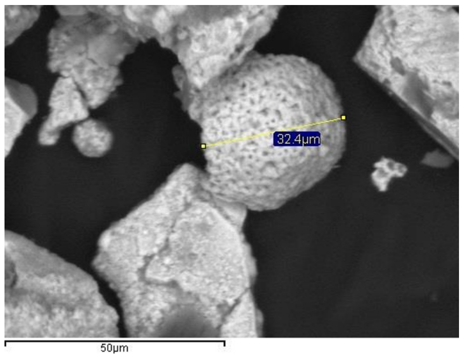
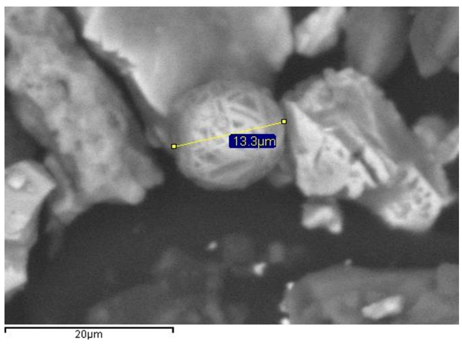


Fig.6. Anthropogenic magnetic particle in the form of sphere and smooth structure from the studied samples of Sarigiol basin.

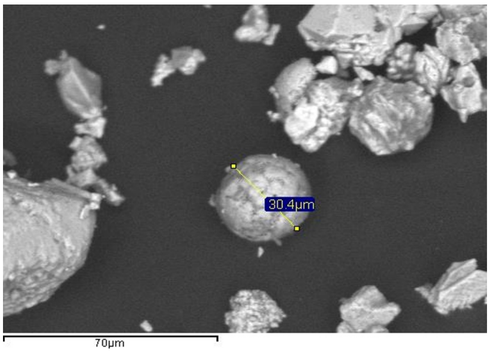


(a)

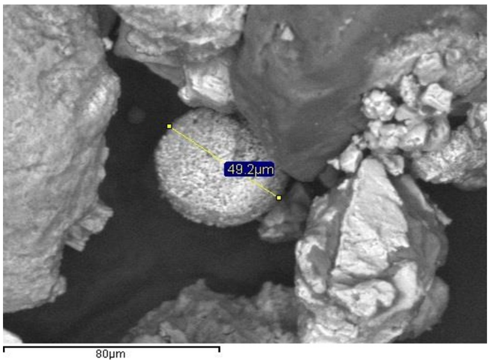


(b)

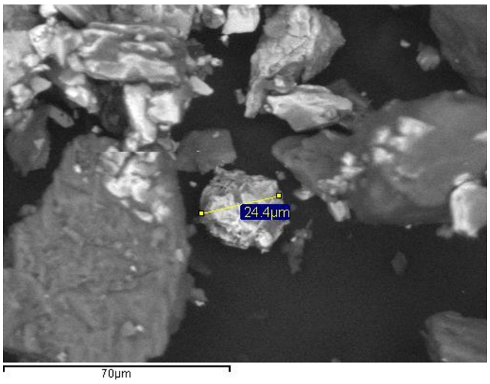
Fig. 7a, b. (a) Coating of anthropogenic magnetic particle in the form of sphere and with orange-peel structure and (b) anthropogenic magnetic particle in the form of sphere and with thread-like surface structure from the studied samples of Sarigiol basin.



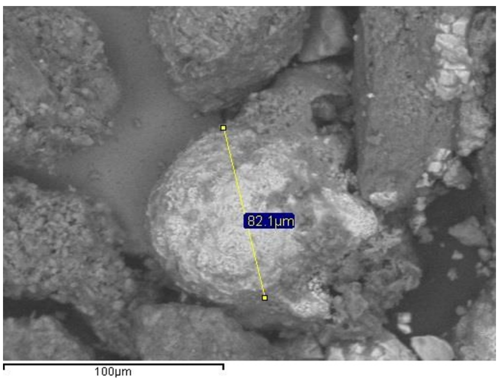
(a)



(b)



(c)



(d)

Fig. 8a-d. Anthropogenic magnetic particle in the form of sphere with (a) blocky-style structure, (b) spongy type structure, (c) a spherule that lost its sphericity and (d) a large spherule in the form of aggregate from the studied samples of Sarigiol basin.

According to the mapping of the ratio of the anthropogenic to lithogenic magnetic particles, the highest values appear extensively at the NE part of the study area (close to the facilities of Agios Dimitrios power station) and locally at the NW, N (S of Kardia power station) and SE part of the basin (Fig.9). Lowest values of the ratio are shown at the centre of the study area. The average value of the ratio is 0.08, in some of the studied samples is 0, while the maximum value is 0.29. The highest values at the NE part of the basin show a tendency to maintain towards Agios Dimitrios power station and additionally, close to two temporary ash deposition sites (Fig.10a, 10b) and the ash transport conveyor belt to the South Field mine that crosses the entire northern side of Sarigiol basin (Fig.2). These high values of the anthropogenic to lithogenic magnetic particles ratio are a strong indication of the effect that anthropogenic activities and specifically the fly ash dispersion, have at the upper soil/sediment horizons of the Sarigiol basin.

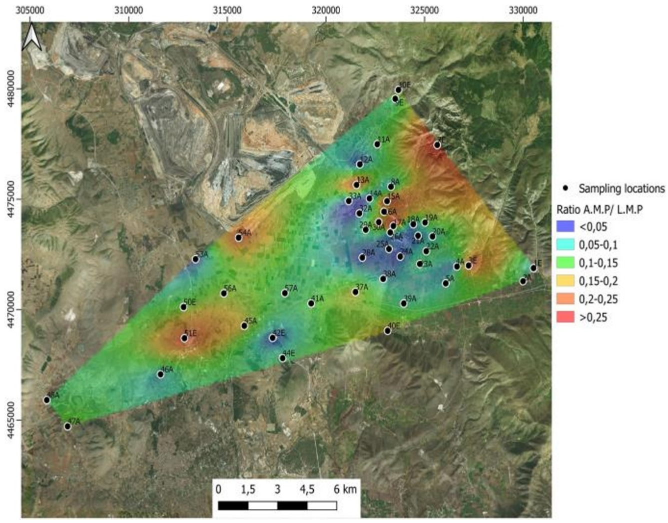
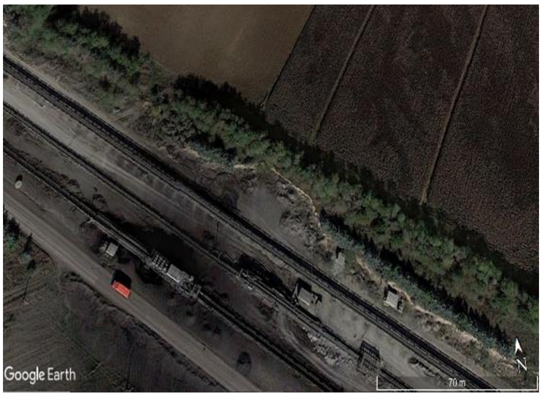


Fig. 9. Spatial distribution of the ratio the anthropogenic to lithogenic magnetic particles (A.M.P/L.M.P) at the study area of Sarigiol basin.

(a)



(b)

Fig. 10a, b. Temporary ash deposition sites NW of Agios Dimitrios power stations.

The constant increase of environmental pollution during the last decades, has triggered the urgent and effective removal or separation of pollutants such as heavy metals. For the study area of Sarigiol basin, deep tilling of the soil in order to be mixed with soil from deeper horizons with possible incorporation of industrial minerals and rocks, e.g. zeolite, could immobilize the pollutants that are present at the upper soil/sediment horizons of the area due to the extensive fly ash dispersion from Agios Dimitrios and Kardia power plants activity.

4 Conclusions

Soil (12) and sediment (47) samples were collected from the Sarigiol basin in order to study the morphological characteristics of their magnetic fraction and depict the spatial distribution of the ratio of anthropogenic to lithogenic magnetic particles. The studied magnetic particles appear in the form of octahedrons and spheres and have lithogenic and anthropogenic origin, respectively. The size of the magnetic spheres is identical to that of the fly ash particles, but the lithogenic magnetic particles tend to have bigger sizes. The complex surface structure of the spheres is proof of fossil fuel combustion at high temperatures.

The source of the lithogenic magnetic particles is the ophiolite complexes at the NE and SW part of the study area while the presence of the spheres may be attributed to the fly ash and its dispersion during transportation from the two power stations Agios Dimitrios and Kardia, located at the research area. Soil permeability and wind direction are factors that enhance the deposition and integration of fly ash. High values of the ratio of anthropogenic to lithogenic magnetic particles show the environmental footprint that anthropogenic activities have at the upper horizons of Sarigiol basin.

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