

MINERALOGICAL COMPOSITION OF SUSPENDED PARTICLES PM10 IN THE PTOLEMAIS-KOZANI AREA, MACEDONIA, GREECE

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Abstract

PM10 suspended particles were collected from the Kardias lignite mine (July 2009), the the campus of Technological Education Institution of Western Macedonia (December 2010) and the Kozani city centre (August 2005). The mineralogical composition and the amorphous materials content of the samples was determined by X-Ray Powder Diffraction method. All samples contain amorphous materials (43-66 wt.%), calcite (13-37 wt.%), micas + clays (4-9 wt.%) and quartz (2-8 wt.%), while in three samples feldspars (2-11 wt.%) were detected. Anhydrite, which is a constituent of the fly ash and the bottom ash, was detected (6 wt.%) only in one sample from the area of Kardias mine. Gypsum was detected, in the Kardias mine (2 and 3 wt.%), in the Kozani city centre (8 wt.%) and in the University campus (13 and 14 wt.%). Gypsum is a constituent of the mined lignite, the stack-gas ash and the Saharan dust. That explains the higher concentrations of gypsum in the University campus on 1st and 2nd of December 2010, where the influence of Saharan dust on the atmospheric particulate matter levels in Western Macedonia was reported.

Keywords: *Atmospheric pollution, Saharan dust, Lignite mining.*

Περίληψη

Αιωρούμενα σωματίδια PM10 συλλέχθηκαν από το λιγνιτωρυχείο της Καρδιάς (Ιούλιος 2009), το δώμα του κεντρικού κτιρίου του ΤΕΙ Δυτικής Μακεδονίας (Δεκέμβριος 2010) και το κέντρο της πόλης της Κοζάνης (Αύγουστος 2005). Η ορυκτολογική σύσταση και η περιεκτικότητα σε άμορφα υλικά προσδιορίστηκαν με την μέθοδο περιθλασιμετρίας ακτίνων Χ κόνεως. Όλα τα δείγματα περιέχουν άμορφα υλικά (43-66 %κ.β.), ασβεστίτη (13-37 %κ.β.), μαρμαρυγίες + αργιλικά ορυκτά (4-9 %κ.β.) και χαλαζία (2-8 %κ.β.), ενώ σε τρία δείγματα ανιχνεύθηκαν άστριοι (2-11 %κ.β.). Ο ανυδρίτης, ο οποίος είναι ένα συστατικό της ιπτάμενης τέφρας και της τέφρας εσχάρας, ανιχνεύθηκε (6 %κ.β.), μόνο σε ένα δείγμα από την περιοχή του ορυχείου Καρδιάς. Η γύψος ανιχνεύθηκε, στο ορυχείο Καρδιάς (2 και 3 %κ.β.), στο κέντρο της πόλης της Κοζάνης (8 %κ.β.) στο δώμα του κεντρικού κτιρίου του ΤΕΙ Δυτικής Μακεδονίας (13 και 14 %κ.β.). Η γύψος

είναι ένα συστατικό του εξορυσσόμενου λιγνίτη, της τέφρας καπναερίων και της σκόνης της Σαχάρας. Αυτό εξηγεί τις υψηλότερες συγκεντρώσεις της γύψου στην περιοχή του ΤΕΙΔΜ στις 1 και 2 Δεκεμβρίου 2010, όπου αναφέρθηκε η επιρροή της σκόνης από τη Σαχάρα στα επίπεδα αιωρούμενων σωματιδίων στη Δυτική Μακεδονία.
Λέξεις κλειδιά: ατμοσφαιρική ρύπανση, σκόνη Σαχάρας, εξόρυξη λιγνίτη.

1. Introduction

The region of Western Macedonia constitutes an interesting and distinct case as far as air pollution is concerned. The main coal mining area in Greece is the Lignite Centre of Western Macedonia (LCWM), in the Florina-Ptolemais-Kozani area. The LCWM produces approximately 50 million tons of lignite annually to feed 6 thermal power plants, with 18 lignite thermal units and with a total installed capacity of 4388 MW. The surface lignite mining requires the excavation of about 315 million m³ of overburden and interbedded sediments per year. The surface mines occupy an area of 160000 hectares. The quality of the lignite is related both to the quality of the organic matter and to the inorganic impurities of the lignite and the nature of the thin intermediate sterile layers, which are co-excavated. Silicates, carbonates, clays, sulphates and oxides dominate the mineral matter in lignite. During lignite combustion the mineral matter of lignite undergoes a series of physical and chemical changes. Some minerals contained in the lignite ashes (fly ash, bottom ash, stack-gas ash), are initial constituents of the mined lignite, while some others are formed during the combustion of the lignite or by the soaking of the fly and bottom ashes with water during its transportation by conveyor belt from the Power Plants to the ash disposal areas (e.g., Filippidis and Georgakopoulos, 1992; Filippidis *et al.*, 1992, 1996; Kassoli-Fournaraki *et al.*, 1992; Kolovos *et al.*, 2002; Kantiranis *et al.*, 2005; Petrotou *et al.*, 2012; Tsirambides and Filippidis, 2012; Nikolaidou, 2014).

Mineral dust is a major contributor to aerosol loading. Varied agricultural and industrial activities constitutes a subject of great interest, mainly the atmospheric burden caused by suspended particles. The problem becomes more complex if we take into consideration the contribution of the urban sources of pollution and the influence of Saharan dust on the atmospheric particulate matter levels in Southern European countries. It is estimated that million tons of desert dust are transported over the Mediterranean sea (e.g., Bergametti *et al.*, 1989; Avila *et al.*, 1997; Rodriguez *et al.*, 2001; Sciare *et al.*, 2003; Moreno *et al.*, 2005; Gobbi *et al.*, 2007; Viana *et al.*, 2007; Remoundaki *et al.*, 2011; Samoli *et al.*, 2011). The new limits of the directive for the quality of air in Europe for PM10 is determined to 50 µg/m³ (Directive 2008/50/EC).

The climate of the area is generally considered to be continental with heavy rains and snowfall and many significant temperature fluctuations. Temperatures are particularly low in the winter, while the summer is cool in the mountains and hot in the plains. Humidity is lower in Kozani which lies on an extended plateau. On the part of the air temperature the coldest month is January and during the summer the hottest one is July. On the part of winds, their flow is forced to follow the topography of the area and the prevailing winds in the valley are generally either North-Northwest or South-Southeast (Nikolaidou, 2014).

The present paper reports on the mineralogical composition of PM10 suspended particles in the industrial axis of Western Macedonia (from north to south): Kardias lignite mine - University of Applied Sciences Western Macedonia campus - Kozani city centre.

2. Materials and Methods

The PM10 suspended particles were collected in teflon filters in three different places and three different periods. In the Kardias lignite mine the 2 samples were collected 17 and 31 July 2009, at the campus of Technological Education Institution of Western Macedonia the 2 samples were collected 1 and 2 December 2010 and at the Kozani city centre the 2 samples were collected 3 and

13 August 2005. During the dates of 1 and 2 December 2010 there was influence of Saharan dust on the atmospheric particulate matter levels of Greece and Western Macedonia.

The PM10 suspended particles were selected by three different stable - portable collectors-stations, positioned in Kardina lignite mine, in the campus of Technological Education Institution of Western Macedonia and in the Kozani city centre. The conducted sampling concerns suspended particles of dust, specifically the ones called PM10 suspended particles having a diameter $< 10\mu\text{m}$.

The mineralogical composition of the samples was determined by X-Ray Powder Diffraction (XRPD) method. The XRPD was performed using a Philips (PW1710) diffractometer with Ni-filtered CuK α radiation. The randomly oriented samples were scanned over the $3\text{-}63^\circ 2\theta$ interval at a scanning speed of $1.2^\circ/\text{min}$. The XRPD conditions were exactly the same for all samples. Semi-quantitative estimates of the abundance of the mineral phases were derived from the XRPD data, using the intensity of a certain reflection, the density and the mass absorption coefficient for CuK α radiation for the minerals present.

In the XRPD patterns the presence of amorphous materials was clear as a broad background hump between approximately 10° and $50^\circ 2\theta$. The semi-quantitative estimation of the percentage of total amorphous materials was achieved by comparing the area of each broad background hump, which represented the amorphous materials in each sample, with the analogous area of standard mixtures of minerals with different contents of natural amorphous material, scanned under the same conditions. The XRPD method is a very good, effective and useful tool for the determination of the percentage of amorphous materials contained in a natural or synthetic sample (Kantiranis *et al.*, 2004, 2005, 2006).

3. Results

The PM10 particles concentration and the semi-quantitative mineralogical composition of the samples are presented in Table 1. In all XRPD patterns the presence of amorphous materials was clear as a broad background hump between approximately 10° and $50^\circ 2\theta$, as well as the reflection of the Teflon filter (Figure 1).

4. Discussion and Conclusions

All samples contain amorphous materials (43-66 wt.%), calcite (13-37 wt.%), micas + clays (4-9 wt.%) and quartz (2-8 wt.%). The term “mica + clays” contains the clay minerals (kaolinite, illite, smectite, vermiculite, palygorskite) and fine micas. In five (5) samples gypsum was detected (2-14 wt.%), in three (3) samples feldspars (2-11 wt.%) and in one (1) sample 6 wt.% anhydrite.

The amorphous materials (organic and inorganic) are contained in the: a) mined lignite, b) fly ash, c) bottom ash, d) stack-gas ash and e) various industrial materials used by man (e.g., Kantiranis *et al.*, 2004, 2005, 2006).

Concerning the minerals of Table 1: a) The fly ash and the bottom ash contain mainly the minerals anhydrite, calcite, quartz, mica + clays and feldspars, b) The stack-gas ash contains mainly calcite and gypsum, c) The mined lignite contains the minerals calcite, mica + clays, quartz, feldspars and gypsum, d) The rocks, sediments, intermediate steriles, soils and building materials of the Florina-Ptolemais-Kozani basin contain the minerals calcite, mica + clays, quartz and feldspars (e.g., Filippidis and Georgakopoulos, 1992; Filippidis *et al.*, 1992, 1996, 1997; Kassoli-Fournaraki *et al.*, 1992, 1993; Triantafyllou *et al.*, 2000; Kolovos *et al.*, 2002; Mouhtaridis *et al.*, 2003; Kantiranis *et al.*, 2004, 2005, 2006) and e) The minerals calcite, mica + clays, quartz, feldspars and gypsum, identified as suspended particles in the Canary Islands (Spain) and the city of Volos (Greece), originate from Sahara (Africa) (e.g., Alastuey *et al.*, 2005; Kandler *et al.*, 2007; Coz *et al.*, 2009; Remoundaki *et al.*, 2011; Kantiranis *et al.*, 2012).

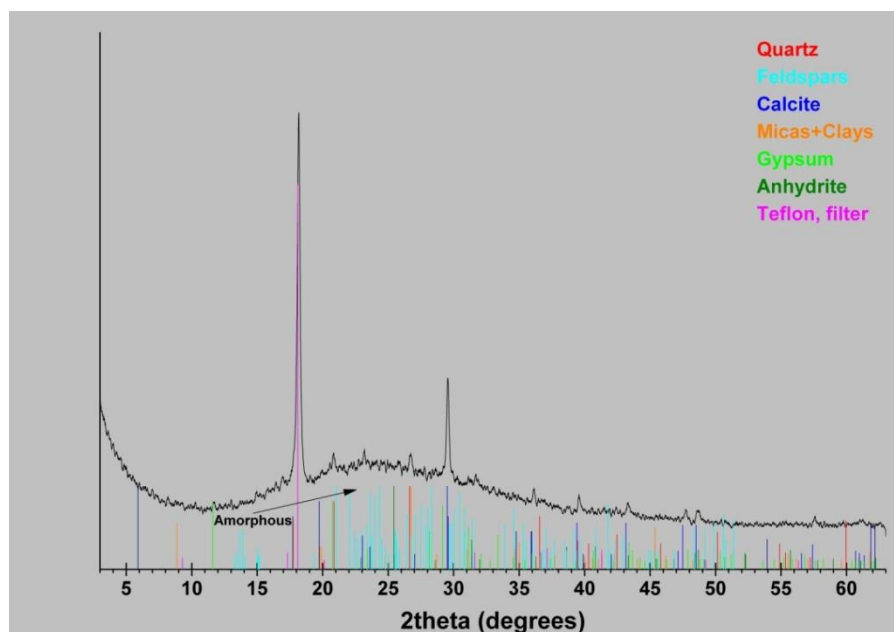


Figure 1 – X-Ray Powder Diffraction pattern of sample NP2348.

Table 1 – PM10 concentration and semi-quantitative mineralogical composition.

Sample No Sampling date Influence	Sampling Place	Amor phous Wt. %	Calcite Wt. %	Mica+ Clays Wt. %	Quartz Wt. %	Gypsum Wt. %	Feldsp ars Wt. %	Anhydri te Wt. %
NP2268 Jul. 17, 2009	Kardia Lignite Mine	51	37	5	2	3	2	-
NP2348 Jul. 31, 2009		55	29	4	2	2	2	6
NP2359 Dec. 1, 2010 Saharan dust	University Campus	43	28	7	8	14	-	-
NP2360 Dec. 2, 2010 Saharan dust		46	26	9	6	13	-	-
NP861 Aug. 3, 2005	Kozani City Centre	50	29	8	5	8	-	-
NP876 Aug. 13, 2005		66	13	6	4	-	11	-

The possible main sources of the minerals of Table 1 are the rocks, sediments, intermediate steriles, soils, building materials, mined lignite, fly ash, bottom ash, stack-gas ash and the Saharan dust. Calcite is a constituent of all sources, quartz, mica + clays and feldspars are constituents of all sources except the stack-gas ash. Anhydrite is a constituent of the fly ash and the bottom ash, while gypsum is a constituent of the mined lignite, the stack-gas ash and the Saharan dust. These explains the mineralogical composition of the Table 1, where anhydrite was detected only in the area of Kardia mine (31 July 2009), while gypsum presents the largest concentrations (13 and 14 wt.%) in

the University campus on 1st and 2nd December 2010, where the influence of Saharan dust on the atmospheric particulate matter levels in Western Macedonia was reported.

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