Seasonal Variations of the Mineralogical Composition and the Organic Matter Content of Falling Dust in Thessaloniki During 2012-13

P. Kollias, N. Kantiranis, I. Pytharoulis and P. Zanis

Abstract The present study examines the annual variation of falling dust particles and their mineralogical composition and organic material in the city of Thessaloniki during June 2012-May 2013. Mineralogical analysis and organic material were conducted in the <63 μm fraction of falling dust samples collected from rooftop levels from three sampling locations, East, Central and West Thessaloniki. This study indicated that calcite and quartz are the major inorganic constituents of the <63 μm fraction, while organic content show increased amount during winter. The latter attributed to the uncontrolled burning of biomass burners for domestic heating.

1 Introduction

The difficult economic effects on urban economy in the last six years in Greece lead the majority of people turn to alternative forms for domestic heating such as the uncontrolled consumption of biomass, i.e. firewood and any other form of artificial substitutes (Kollias et al. 2014). The particles released from burning wood contain organic toxic ingredients such methylphenol (Kjällstrand and Petersson 2001) and polycyclic aromatic hydrocarbons (Barregard et al. 2006). Numerous studies have certified that biomass burning contributes as a release source of fine particles PM2.5 (e.g. Zheng et al. 2005; Verma et al. 2009, Daher et al. 2012; Saffari et al. 2013).

Exposure to emissions from biomass combustion leads to particular adverse health effects such as cardiorespiratory problems, increased blood pressure, increased mortality/decrease of life expectancy, lung disorders and lung cancer,

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systemic inflammation and oxidative stress (Barregard et al. 2006; Orozco -Levi et al. 2006; McCracken et al. 2007; Mousiopoulos 2013; Saffari et al. 2013).

One of the biggest problems of air pollution in the city of Thessaloniki is the high concentrations of suspended particles. Airborne particles vary in terms of their concentration, and physical, chemical and morphological characteristics (Samara et al. 2011). Emitted primary (anthropogenic processes, soil erosion, sea droplets) and suspended directly in the atmosphere in particulate form, either produced secondarily in the atmosphere (condensation, nucleation, chemical conversion). Suspended particles with equivalent aerodynamic diameter less than 10 μm (PM10, respirable suspended particulates) can act as carriers for various chemical compounds for biological contaminants adsorbed or adhered on them, as well as catalysts of chemical reactions that occur in the atmosphere, which mainly contribute to air pollution. These particles are separated into particles having diameter less than 2.5 μm (fine particles) and greater than 2.5 μm (coarse particles). Airborne particles of diameter less than 2.5 μm are able to enter the respiratory system and then via the lungs into the bloodstream.

High concentrations of suspended particles at ground level occur during smog conditions, in association with high levels of sulfur dioxide, or with photochemical pollutants such as O_3, NO_2, PAN, etc. The most intense incidents of smog formation occur in urban areas, where light winds and a shallow boundary layer air act combined resulting to concentration of pollutants in a relatively small volume of air. The weather-meteorological conditions enhance the formation of this kind of cloud that usually occurs during the winter period in early morning hours (Kourtidis et al. 2002; Marley and Frederick 2008).

The present study examines the impact of air pollutants in the atmosphere of Thessaloniki during years 2012-13. Mineralogical and organic material analysis was implemented on falling dust collected at building rooftop level from three sampling location areas that are Kalamaria (East Thessaloniki), Aristotle University (center of Thessaloniki) and Seaport (West Thessaloniki).

2 Methodology

2.1 Sampling and Sample Preparation

Falling-dust samples collected at rooftop building level from three selected sampling sites in Kalamaria district (multi-storey building), Aristotle University (building roof of the Faculty of Sciences) and Seaport (multi-storey parking lot station). Sampling was carried out during the period June 2012–May 2013 between 23:00 to 00:00, twice a month every 15 days. From each sample 50–150 g of powder was collected, wiping an area of 1 m^2 using sterilized collectible instruments. The samples were dried in an oven at 35 °C for 3 days. After that the < 63 μm fraction was separated by sieving for further investigation. A total

number of over 70 samples (3 sampling locations × 2 samples per month × 12 months = 72 samples) were collected between June 2012 and May 2013.

2.2 Analytical Methods

The mineralogical composition of the studied samples was determined by X-ray Powder Diffraction (XRPD) method. The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuKα radiation on randomly oriented samples. The counting statistics of the XRPD study were: step size: 0.01° 2θ, start angle: 3°, end angle: 63° and scan speed: 0.02° 2θ/s. Quantitative estimates of the abundance of the mineral phases derived from the XRPD data, using the intensity of a certain reflections and external standard mixtures of minerals (Kantiranis et al. 2004). The proportion of amorphous material (organic and inorganic origin) was calculated according to the methodology described by Kantiranis et al. (2004).

The calculation of the contained organic material was determined in each according to Jackson (1974) with the effect of an aqueous solution 30 % H_2O_2 in a representative sample of the <63 μm fraction.

3 Results and Discussion

3.1 Mineralogical Analysis and Organic Material

In Table 1 the mean value, standard variation, minimum and maximum amounts of the minerals and the amorphous content determined in the <63 μm sample fraction are shown. Also, the weight and the organic material of the <63 μm fraction are given. More specifically, the <63 μm fraction of the total amount of falling dust during 2012–13 ranged from 10.3 % (Autumn 2012) to 27.5 % (Spring 2013). It is clear from Fig. 1 that the mean weight of the <63 μm fraction is progressively increasing from Summer 2012 to Spring 2013. Kollias et al. (2014), comparing the periods of December 2011 and December 2012, found an incensement in the amount of <63 μm fraction of falling dust during December 2012 in the same sampling sites and attributed this observation to favorable meteorological conditions with atmospheric stability and low winds.

According to the results of the mineralogical analysis (Table 1), the samples of falling dust primarily consist of calcite (35–45 wt%) and quartz (29–35 wt%) as major phases, feldspars and dolomite in lesser percentages, while mica, clay minerals and amphibole were detected in very small quantities. Gypsum was measured at low amounts in Spring 2013. Furthermore, significant amounts of amorphous phases were identified (7–15 wt%).

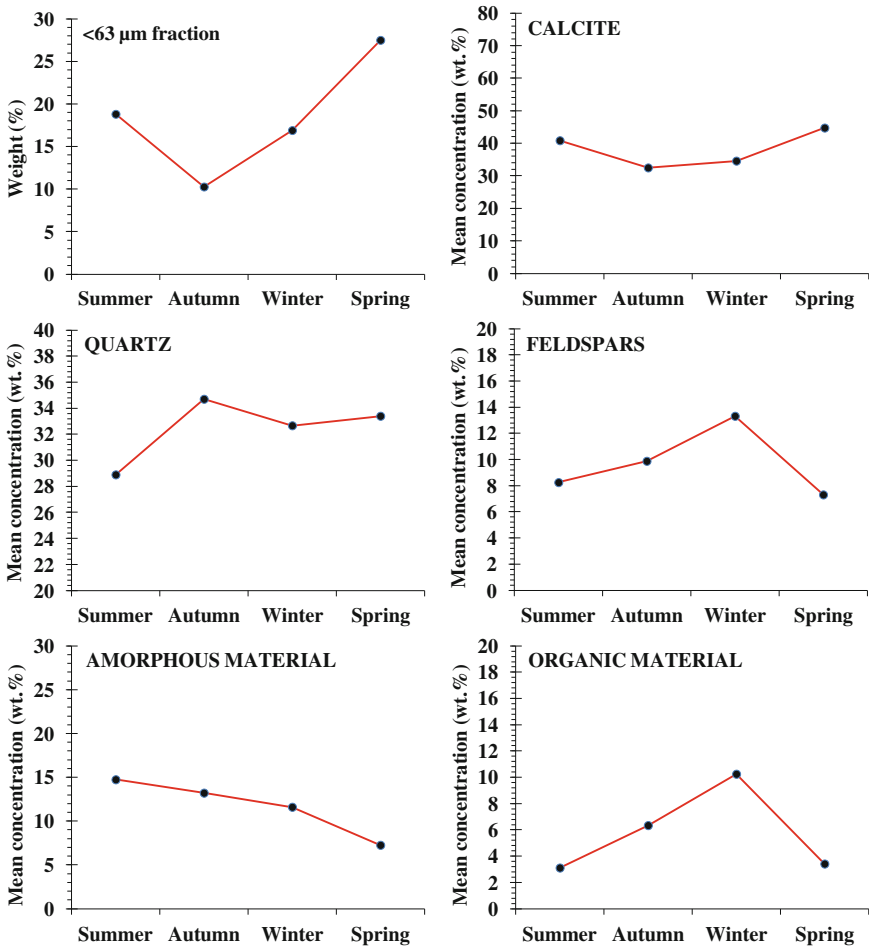

Fig. 1 Annual variation (wt. %) of the weight and the amounts of calcite, quartz, feldspars, amorphous and organic material of the <63 μm fraction of the studied samples

Quartz (SiO_2) is one of the most resistant mineral to the physical and chemical erosion. The possible effects of the crystalline forms of silica (most common quartz) on health are of particular interest (Ikeda et al. 1986), while the International Agency for Research on Cancer (1997) classifies them as carcinogenic to humans (Category I). Also, calcite, dolomite, feldspars and gypsum derived probably from the erosion of building materials (Tossavainen and Forrssberg 1999).

The phyllosilicate minerals (mica and clay minerals) may possibly be derived from the corrosion of construction materials and deposited directly on the ground, but it is probably due to their lamellar structure and low specific weight can be carried out by re-suspending from other regions. The amorphous phases derive from the

Table 1 Weight (%) of the <63 μm fraction, semi-quantitative mineralogical composition (wt%) and organic matter (wt%) of the studied samples

		Summer 2012				Autumn 2012				Winter 2012–13				Spring 2013			
		MV	*SD*	Min	Max	MV	*SD*	Min	Max	MV	*SD*	Min	Max	MV	*SD*	Min	Max
Weight of the <63 μm fraction	g/m^2	0.74	*0.43*	0.24	1.52	0.81	*0.22*	0.56	0.99	0.94	*0.63*	0.42	1.82	2.69	*2.81*	0.71	7.60
	%	18.8	*13.2*	6.7	48.7	10.3	*6.0*	6.1	17.2	16.9	*11.9*	6.9	34.1	27.5	*28.6*	5.2	69.9
Quartz		29	*7*	21	44	35	*9*	24	40	33	*11*	24	47	33	*6*	23	41
Micas		1	*0.5*	1	2	1	*0*	1	2	1	*0*	1	1	1	*1*	1	2
Clay minerals		2	*1*	1	3	3	*1*	1	3	2	*1*	1	2	2	*1*	1	4
Feldspar		8	*4*	3	13	10	*1*	9	11	13	*7*	8	24	7	*5*	3	13
Calcite		41	*4*	33	46	32	*12*	24	46	35	*12*	22	48	45	*9*	31	59
Dolomite		4	*1*	2	7	5	*2*	4	7	4	*1*	3	5	3	*1*	3	4
Amphibole		2	*1*	1	2	2		2	2	2	*1*	1	2	1	*0.5*	1	2
Gypsum		–	–	–	–	–	–	–	–	–	–	–	–	1	*0*	1	1
Amorphous		15	*6*	8	27	13	*4*	9	16	12	*3*	8	16	7	*2*	3	9
Organic matter		3	*1*	2	5	6	*2*	4	8	10	*3*	7	14	3	*1*	2	4

MV Mean value, *SD* Standard deviation, *Min* Minimum value, *Max* Maximum value

incomplete combustion of organic material (mainly solid and liquid fuels) and from the corrosion of inorganic aluminosilicate phases of buildings components.

The organic material was measured at concentrations between 3 wt% (Summer 2012 and Spring 2013) and 10 wt% (Winter 2012–13) showing significant differences between seasons. Specifically, in the samples collected during Winter higher participation of organic material was found. During Winter 2012-13, the mean amount of organic matter is more than 3 times higher compared with Summer 2012 and Spring 2013 and more than 1.5 times higher compared with Autumn 2012. Kollias et al. (2014) found higher amounts of organic material comparing December 2012 with December 2011 and September 2012 and conclude that this can be attributed to the extensive and uncontrolled burning of biomass for domestic heating. Petrakakis et al. (2013) found increased concentrations of particulate matter in Thessaloniki during the Winter period after 2010 which attributed to the burning of wood and other types of biomass. According to Moussiopoulos (2013) the burning of biomass and wood led to a rapid increase in the average monthly concentration of fine particles in the Winter period (Nov 2012–January 2013), with this increase being more pronounced in afternoon hours. Moreover, Saffari et al. (2013) found that in the urban background of Thessaloniki's region concentrations of PM2.5 in the Winter of 2013 were 30 % higher compared to the same period in 2012 and 2–5 times higher concentrations of the biomass combustion indicators such as water-soluble K, anhydrides sugars, organic carbon and PAHs.

4 Conclusions

Mineralogical analysis and organic material of the falling dust samples collected from rooftops in three sampling sites during Summer 2012-Spring 2013 from three sampling sites in the wider conurbation of Thessaloniki found that:

- The fallen dust mainly consists of inorganic origin components from the corrosion of building materials without excluding material contribution from air suspending fumes.
- Calcite and quartz are the major inorganic crystalline phase determined with the latter to be potentially dangerous for public health.
- A significant increase in the organic load of dust samples had been observed for Winter 2012–13 compared to the other seasonal sampling periods and to previous Winter and Autumn monthly periods
- The pollution impact of the atmosphere of Thessaloniki with pollutants of organic origin during the Winter 2012–13 attributed to the extensive and uncontrolled burning of biomass for domestic heating. This is a consequence of the economic crisis in Greece and the high value of petroleum fuel during this period.

References

Barregard L, Sällsten G, Gustafson P, Andersson L, Johansson L, Basu S, Stigendal L (2006) Experimental exposure to wood smoke particles in healthy humans: Effects on markers of inflammation, coagulation, and lipid peroxidation. Inhal Toxicol 18(11):845–853. doi:10.1080/08958370600685798

Daher N, Ruprecht A, Invernizzi G, De Marco C, Miller-Schulze J, Heo JB, Shafer MM, Shelton BR, Schauer JJ, Sioutas C (2012) Characterization, sources and redox activity of fine and coarse particulate matter in Milan, Italy. Atmos Environ 49:130–141. doi:10.1016/j.atmosenv.2011.12.011

Ikeda M, Watanabe T, Hayashi H, Tsunoda A (1986) Toxicological evaluation of quartz and silica contents in studded tire-generated dust in the city of Sendai. Tohoku J Environ Med, 148: 207–211. http://doi.org/10.1620/tjem.148.207

International Agency for Research on Cancer (1997) Silica, some silicates, coal dust and para-aramid fibrils. Int Agency Res on Cancer (IARC) Monographs, 68, 506

Jackson ML (1974) Soil chemical analysis. Adv. Coarse, Madison, Wisconsin 690 pp

Kantiranis N, Stergiou A, Filippidis A, Drakoulis A (2004) Calculation of the percentage of amorphous material using PXRD patterns. Bull Geol Soc of Greece 36:446–453

Kjällstrand J, Petersson G (2001) Phenolic antioxidants in wood smoke. Sci Total Environ 277(1–3):69–75. doi:10.1016/S0048-9697(00)00863-9

Kollias P, Kantiranis N, Samara C, Zanis P, Pytharoulis I (2014) Impact of uncontrollable burning of biomass for residential heating in the atmosphere of the city of Thessaloniki during December 2012. In: 5th Environmental Conference of Macedonia, Thessaloniki, March 14_16, 2014, e-Proc

Kourtidis K, Ziomas I, Zerefos C, Kosmidis E, Symeonidis P, Christophilopoulos E, Karathanassis S, Mploutsos A (2002) Benzene, toluene, O_3, NO_2 and SO_2 measurements in an urban street canyon in Thessaloniki, Greece. Atmos Environ 36:5355–5364. doi:10.1016/S1352-2310(02)00580-0

Marley A, Frederick JE (2008) Formation and Effects of Smog. Environmental and Ecological Chemistry—vol. ii—©Encyclopedia of Life Support Systems (EOLSS)

McCracken JP, Smith KR, Diaz A, Mittleman MA, Schwartz J (2007) Chimney stove intervention to reduce long-term wood smoke exposure lowers blood pressure among Guatemalan women. Environ Health Persp 115(7):996–1001. doi:10.1289/ehp.9888

Mousiopoulos N (2013) Impact of biomass burning and wood in air quality: measurements and simulations' Greek International University workshop titled: Economic Crisis and Energy Mix: Societal and Health Impact of Biomass and Wood Burning, Thessaloniki, 16/12/2013

Orozco-Levi M, Garcia-Aymerich J, Villar J, Ramirez-Sarmiento A, Anto JM, Gea J (2006) Wood smoke exposure and risk of chronic obstructive pulmonary disease. Eur Respir J 27(3):542–546. doi:10.1183/09031936.06.00052705

Petrakakis MJ, Kelessis AG, Tzoumaka PN. Samara C (2013) Levels of suspended particulate matter before and after the economic crisis in Thessaloniki, Greece. In: 17th International MESAEP Symposium Istanbul/Turkey, September 28 to October 1

Saffari A, Daher N, Samara C, Voutsa D, Kouras A, Manoli E, Karagkiozidou O, Vlachokostas C, Moussiopoulos N, Shafer MM, Schauer JJ, Sioutas C (2013) Increased biomass burning due to the economic crisis in Greece and its adverse impact on wintertime air quality in Thessaloniki. Environ Sci Technol 47(23):13313–13320. doi:10.1021/es403847h

Samara C, Argiropoulos A, Grigoratos T, Kantiranis N, Papadopoulou L (2011) Chemical and mineralogical composition of particulate matter PM10 in Thessaloniki. In: 21st Pahellenic Chemistry congress, Thessaloniki, e-proc, 6

Tossavainen M, Forssberg E (1999) The potential leachability from natural road construction materials. Sci Total Environ 239:31–47. doi:10.1016/S0048-9697(99)00283-1

Verma V, Polidori A, Schauer JJ, Shafer MM, Cassee FR, Sioutas C (2009) Physicochemical and toxicological profiles of particulate matter in Los Angeles during the October 2007 Southern California wildfires. Environ Sci Technol 43(3):954–960. doi:10.1021/es8021667

Zheng M, Salmon LG, Schauer JJ, Zeng L, Kiang CS, Zhang Y, Cass GR (2005) Seasonal trends in PM2.5 source contributions in Beijing, China. Atmos Environ 39(22):3967–3976. doi:10.1016/j.atmosenv.2005.03.036