

AIR QUALITY IN MINING AREAS: THE CASE OF STRATONI, CHALKIDIKI, GREECE

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Abstract

Air quality sampling tests are conducted on a 24h basis by “HELLENIC GOLD S.A.” in the Stratoni mining settlement. The settlement is located in the neighbourhood of a flotation plant where galena and sphalerite concentrates are produced after crushing and processing of Pb-Ag-Zn sulfide ore. Old piles of mineral waste occur close to the settlement. The mineralogy of mineral dust collected on filters of 3 air samplers from August to December 2008 was studied. Elemental analysis of mineral dust collected from January to December 2008 was conducted. The purpose of the study was to determine levels of air pollution, type of mineral particles as well as potential sources. Measurements of air quality included PM_{10} . Statistical analysis of the collected data included tests to determine the control on daily particle concentration and mineralogy of fluctuations of temperature, humidity, wind direction and wind speed. Air quality was better than during 1998-2000. Air quality was typically at its worse during hot summer days when wind speed was high. The concentration of PM_{10} particulate matter was quite low when compared to International Air Quality Standards regulations, indicating that levels of air pollution in the area do not pose human health hazards.

Key words: *air quality, mineral dust, PM_{10} , Stratoni, Chalkidiki, Greece.*

1. Introduction

Protection of public welfare from particulate matter in the atmosphere is promulgated by the Greek law and is being monitored by competent agencies based on international air quality standards. Particulate matter is a significant category of pollution with a variety of shapes and sizes, coming from the processing of materials, procedures of combustion and transformation reactions of gas (Cooper & Alley, 2004). Historically, particulate matter (PM) measurements have focused on Total Suspended Particulates (TSP). Last decade the primary air quality standard TSP was replaced with PM_{10} standard. PM_{10} denotes particulate matter which passes through a size-selective inlet as defined in the reference method for sampling and measurement of PM_{10} EN 12341, with a 50% efficiency cut-off at 10 μ m aerodynamic diameter (Directive 2008/50/EC). Recent trends lead to further replacement of PM_{10} by a $PM_{2.5}$ standard. Areas in the country with potential for high levels of mineral particulate matter are those where mining, transportation, deposition, crushing-milling and processing of minerals were conducted (e.g. the Florina – Ptolemais – Kozani lignite basins (Triantafyllou, 2000; Triantafyllou et al., 2000) and Lavrion (Skarpelis et al., 2009).

The examination of the amount and type of the particulate matter is imposed especially in areas

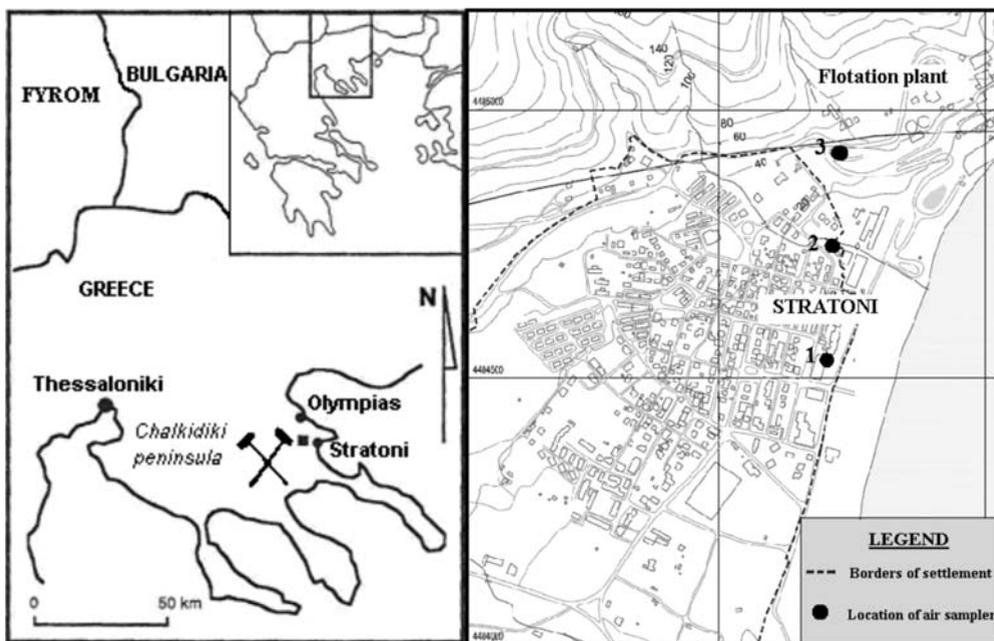


Fig. 1: a: Location of the main mining centers in NE Chalkidiki. b: Location of air samplers. (Ballas & Gazea, 2009).

where grains of minerals with toxic elements load are released by human activities. The mineralogy, chemistry, solubility and oxidation state of the inhaled particles strongly influence human health effects (Posfai & Molnar, 2000; Plumlee et al., 2006).

The wider area that Stratoni settlement belongs to, is well known as “Kassandra Mines” (Fig. 1a). The flotation plant of the mining company “HELLENIC GOLD S.A.” is located at the northeastern part of the Stratoni settlement, producing sphalerite and galena concentrates after processing of Pb-Ag-Zn sulphide ore exploited at the Mavres Petres mine. A crushing-milling facility and condensation-filtration and mineral waste units are associated with the flotation plant. For the protection of the citizens and workers welfare of Stratoni, the company has established and operates three air samplers; location of the samplers is shown in Fig. 1b. Previous studies reported on ambient concentrations of Total Suspended Particulate Matter (TSP) in the wider area of Stratoni (Gaidajis, 2003).

The purpose of this study is to identify the mineral phases of PM_{10} fraction of the dust and search for the source(s) of grains, taking into consideration the chemistry of dust samples and meteorological parameters. Also, there was an evaluation of the impact on air quality at the Stratoni settlement and the data was compared with the conditions during 1998-2000. This data can be used for further assessments of particles dissemination.

2. Geology of the ore deposits

The Kassandra mining district comprises mainly Pb-Zn (Ag-Au) carbonate hosted replacement, skarn and porphyry Cu-Au ore deposits. They are hosted by lithologies of the Serbomacedonian Belt and temporally and spatially related to Tertiary intrusives. The Mavres Petres, Madem Lakkos and Stratoni deposits are structurally controlled by the NW-SE trending Varvara - Stratoni fault and litho-

logically by marble in contact with gneiss of the polymetamorphic Vertiskos Unit. Base metal sulphides, sulphosalts, quartz, rhodochrosite, graphite, kaolinite, sericite are the predominant hypogene minerals (Nikolaou, 1960; Kockel et al., 1977; Nebel et al., 1991; Gilg, 1993; Gilg & Frei, 1994).

3. Materials and Methods

In order to monitor the ambient air quality at Stratoni, air samplers produced by “Thermo Electron” are used (type rp Patrisol –plus model 2025 sequential air sampler). The filters that are used (Pallflex TX40) retain particles PM_{10} , have a diameter of 47mm and are made of glass fiber coated with Teflon and manufactured by Thermo Electron 9. Estimation of the index “Mass Concentration”, indicating the amount of dust deposited on the filter, was made using the formula: $MC = DW \cdot 10^6 / V$, where: MC: Mass Concentration, DW: mass concentration in grams (g) on the surface of the filter and V: volume of air (in m^3) that passed through the filter. Elemental analysis of collected PM_{10} for Pb, Zn, As, Cd, Fe, Cu, Mn, was performed using Inductively Coupled Plasma - Atomic Emission Spectrometry at the laboratories of «HELLENIC GOLD S.A.».

Mineral investigation was carried out with the aid of a reflected light microscope and a JEOL JSM 5600 Scanning Electron Microscope at the Faculty of Geology and Geoenvironment, University of Athens. Mineral examination was conducted on 61 filters, which were chosen based on their high values of mass concentration. Approximately two filters per week were investigated for a six-month period. The mineralogical composition of samples of mineral waste and tailing, stockpiled sulphide ore and dust from the crushing-milling facility, has been also investigated. Emphasis was given on mineral grains of a size $<10\mu m$.

4. Results and Discussion

Based on the measurements of the mass concentration for the year 2008, it is presumed that there is a wide range of values between 2.5 and $79.6\mu g/m^3$ (Table 1).

Although the mass concentration data (Tables 1, 2) refer to PM_{10} and TSP respectively, a trend for reduction of emission of mineral particulates from the time period of 1998-2000 to 2008 is evident. It is worth mentioning that the ratio PM_{10}/TSP is not known; however the mineralogical study of TSP dust collected on the filter of a portable dust sampler during this sampling survey indicates the ratio PM_{10}/TSP is roughly around 0.7.

According to data on Table 1, during 2008, the number of days when mass concentration exceeded the daily limit value of $50\mu g/m^3$, were seven (7) in air sampler SAM 1, two (2) in the air sampler SAM 2 and nineteen (19) in the air sampler SAM 3, indicating that the daily concentration of particulate matter of PM_{10} was quite low when compared to European and International Air Quality Standards. It is worth mentioning – although not directly comparable – that many European cities (e.g. Berlin) cannot comply with the daily limit value for PM_{10} , which is in force since 2005. As stated by Goergen and Lambrecht (2007) Berlin experienced particle episodes in February, March and October during the year 2005 with PM_{10} concentrations up to $130\mu g/m^3$ in two sites, one close to a very busy street downtown and the other at the periphery of the city.

It is noticeable that mass concentration is not always analogous with the amount of mineral grains. This fact can be explained because organic substances from oil combustion as well as particles of biological origin can settle on the surface of the filter.

The examination of the mineralogy of the dust settled on the filters of the air samplers SAM 1-3,

showed that grains of pyrite, galena and sphalerite predominate. At a lower proportion, grains of arsenopyrite, chalcopyrite, barite, cerussite, gypsum, goethite, tennantite, boulangerite and bournotite can be found (Fig. 2a,b and 3b). Furthermore, in some of the filters, grains of halite were identified (Fig. 3a).

Sphalerite, pyrite, galena and arsenopyrite are the predominant minerals in samples collected from mine waste and tailing piles at the vicinity of the processing plant. Minor mineral constituents are gangue minerals (e.g. quartz, sericite, kaolinite). Samples of dust collected within the area of the crushing –milling facility comprise grains of sphalerite, galena and pyrite. Calcite, quartz and feldspars are subordinate.

Table 1. Mass Concentration variation of PM10 dust at Stratoni from January to December 2008.

SAM 1 to SAM 3: Air samplers; Mass Concentration in $\mu\text{g}/\text{m}^3$; NED: Number of Exceedance of regulatory limit Days (35 per year are permitted)

Month	1	2	3	4	5	6	7	8	9	10	11	12	Annual	NED
SAM 1														
min	8.9	18	5.4	8.7	8.3	7.1	8.7	18	12	10	5	2.5	2.5	7
max	38	71	53	64	32	38	29	53	38	50	52	46	70.8	
average	26	33	30	28	17	20	19	31	25	27	24	21	24.6	
median	28	30	28	25	17	20	19	30	23	26	22	17	22.5	
SAM 2														
min	13	20	12	19	11	10	15	13	16	7.5	9.1	3.3	3.3	2
max	27	48	64	29	42	37	27	50	44	52	49	36	63.5	
average	19	29	29	24	22	21	20	34	29	27	24	16	24.8	
median	18	27	29	23	21	19	20	37	29	29	20	15	23.6	
SAM 3														
min	7.6	19	12	9.6	5	11	15	20	6.2	12	3.8	6.7	3.8	19
max	34	55	60	80	75	61	75	63	52	48	46	67	79.6	
average	22	35	33	34	33	33	35	35	28	27	30	23	30.1	
median	20	35	35	30	31	32	31	35	27	27	22	20	27.1	

Table 2. Mass concentration of Total Suspended Particulate matter from 1998 to 2000 (Gaidajis, 2003).

Sampler	Mass concentration ($\mu\text{g}/\text{m}^3$)				
	Number of samples	max	min	average	median
SAM 1	20	100.4	19.1	51.4	54.9
A*	13	106.6	23.2	60.1	57.1
B**	14	185.4	4.8	56.3	39.6

* Sampler close to fuel tanks; ** Sampler close to adit +410

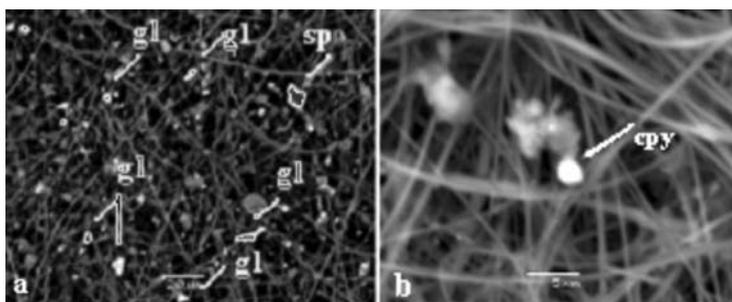


Fig. 2: SEM micrograph of dust grains on air filters: a. “SAM 3 14/9-15/9”, b. “SAM 2 30/9-1/10” (gl: galena, sp: sphalerite, cpy: chalcopyrite).

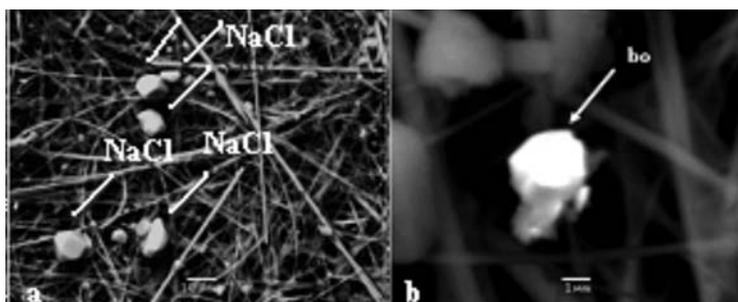


Fig. 3: SEM micrograph of dust grains on air filters: a. “SAM3 14/9-15/9”, b. “SAM3 25/11-26/11” (NaCl: halite, bo: bournonite).

Lead concentration in particulate matter during 2008 can be seen in Table 3. The Pb values are lower than the permitted limit (annual value $0.5 \mu\text{g}/\text{m}^3$; Directive EE 2008/50). It is well-known that due to differential toxicity, various minerals have different impact on human health when inhaled. According to Plumlee et al. (2006), Pb as a constituent of cerussite (a very acid-soluble lead carbonate), Pb oxides, and Pb sorbed onto atmospheric aerosols generated by lead-zinc smelting is substantially more bioaccessible than Pb as a major constituent of galena and various lead-phosphate minerals. Consequently, the dominant presence of galena in the dust acts more positively for the environment rather than other Pb-minerals.

The average concentration of Fe, As, Zn, Cu, Mn and Cd in particulate matter PM_{10} from all air samplers during 2008 is shown in Table 4, whereas the average concentrations of these metals for TSP during 1998-2000 in Table 5. By comparing these concentrations we cannot observe any significant differences. An exception is Fe, which has high levels during 2008 in all air samplers.

Concentrations of the elements Pb, Zn, As, Cd, Fe, Cu, Mn and the Mass Concentration of PM_{10} during 2008 vary widely. It is ascertained that during warm periods the levels of element and mass concentrations are generally higher (Papastamatiou, 2009). This variation can be explained due to high-speed winds, during warm periods and low precipitation, during a major part of the cold period¹.

An effective way to determine the source of metallic minerals in the dust, are wind rose diagrams in connection with the concentrations of chemical elements. In Fig. 4 the average wind direction can

¹ Months from April to October are warm period, whereas November to March are cold period.

Table 3. Pb concentration ($\mu\text{g}/\text{m}^3$) in PM_{10} during 2008.

<i>Sampler</i>	<i>Max</i>	<i>Min</i>	<i>Average</i>	<i>Median</i>
SAM 1	1.116	0.029	0.356	0.257
SAM 2	0.404	0.057	0.184	0.167
SAM 3	0.114	0.013	0.063	0.062

Table 4. Average metal concentration in PM_{10} during 2008

<i>Sampler</i>	<i>Average metal concentration ($\mu\text{g}/\text{m}^3$)</i>					
	<i>Fe</i>	<i>As</i>	<i>Zn</i>	<i>Cu</i>	<i>Mn</i>	<i>Cd</i>
SAM1	1.698	0.174	0.723	0.017	0.167	0.012
SAM2	1.604	0.08	1.178	0.017	0.036	0.011
SAM3	1.379	0.077	0.982	0.009	0.022	0.01

Table 5. Average metal concentration in TSP during 1998-2000 (Gaidajis, 2003)

Location of samplers: A. Close to fuel tanks, B. Close to Adit +410.

<i>Sampler</i>	<i>Average metal concentration ($\mu\text{g}/\text{m}^3$)</i>					
	<i>Fe</i>	<i>As</i>	<i>Zn</i>	<i>Cu</i>	<i>Mn</i>	<i>Cd</i>
SAM 1	0.254	0.012	0.083	0.112	0.055	0.0006
A	0.584	0.045	0.299	0.066	0.121	0.016
B	0.247	0.019	0.051	0.041	0.103	0.0004

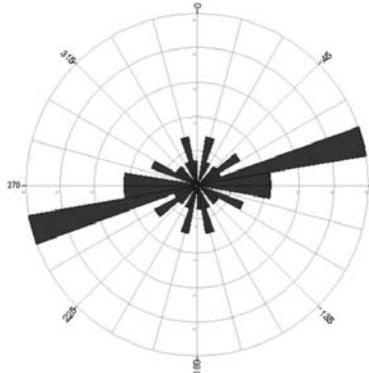


Fig. 4: Wind rose diagram during 2008 in Stratoni (Data from air sampler SAM 1).

be shown as a function of geographical bearings. The length of the bar for a particular direction indicates the time that the wind blows from that direction. It is concluded that the predominant wind direction is ENE and WSW.

Wind rose diagrams were also constructed based on wind data of air sampler SAM 1 and elemental concentrations from chemical analysis of the filters of the same sampler (Fig. 5). The elements Pb and As have the highest concentrations when N-NE directed winds blow, indicating that the main source

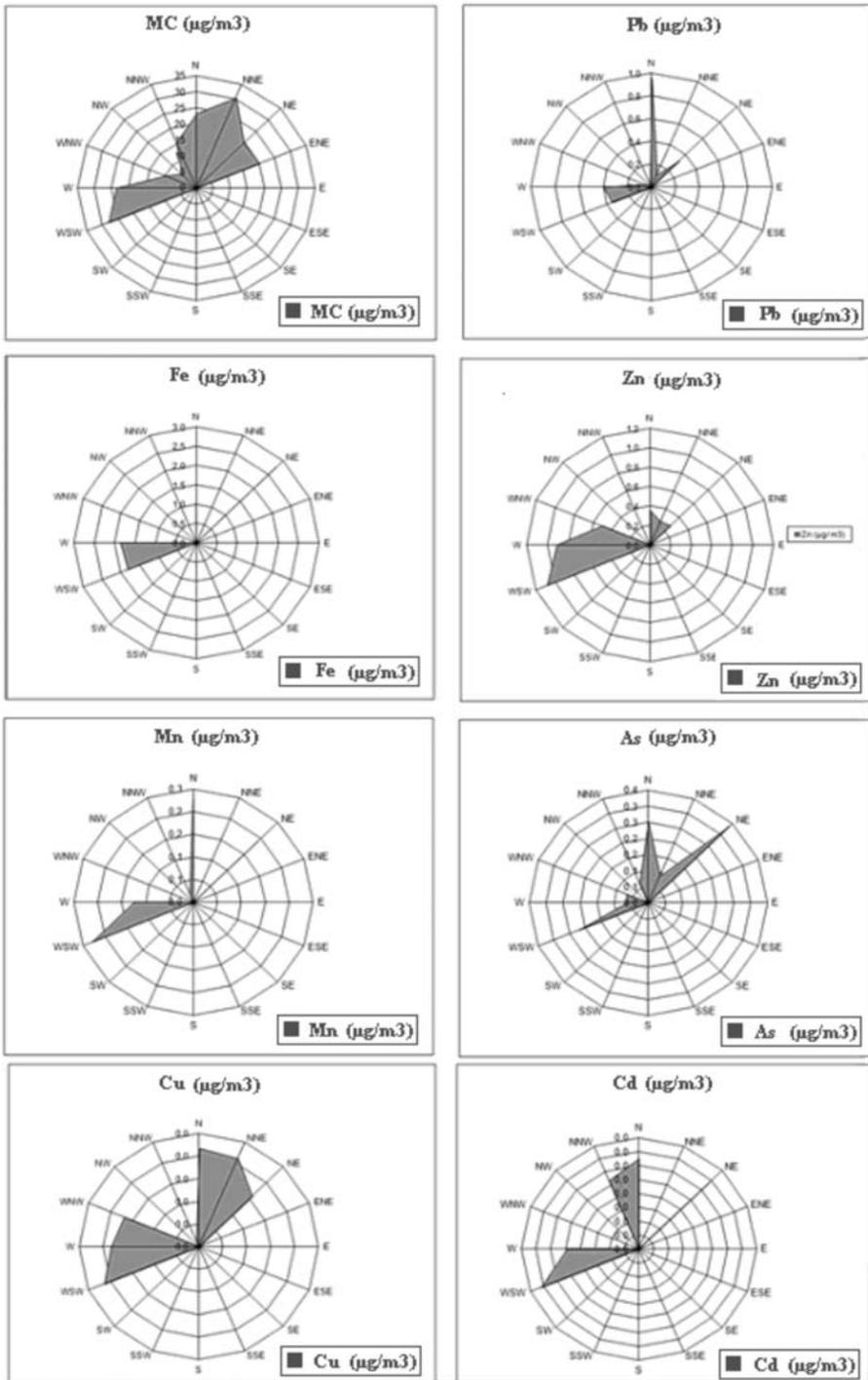


Fig. 5: Wind rose diagrams of PM_{10} , Pb, Fe, Zn, Mn, As, Cu, Cd ($\mu\text{g}/\text{m}^3$) (Data from sampler SAM 1).

of these elements is dust that comes from the processing facilities located on this direction in relation to air sampler SAM1. Wind rose diagrams of Fe, Mn and Zn have high concentrations during W-WSW winds. This observation suggests that the main source of the metal bearing particulate matter is the surface cover of the settlement of Stratoni. Data from previous studies, examining the composition of the soil from gardens of the settlement, confirmed that the main phases are oxides of Fe and Mn (Plakaki, 2006, Argyraki et al., 2007, Nicolaou, 2007). These mineral phases act as collectors for other metals. Finally, Mass Concentration, Cu and Cd, present high concentrations both when NNE and WSW directed winds blow, suggesting a mixed source of the transported particulate matter.

5. Conclusions

Measurements of ambient concentrations of particulate matter of less than 10µm aerodynamic diameter (PM₁₀) are conducted on a 24 hours basis at Stratoni settlement. Evaluation of chemical data from air filters for the year 2008, combined with detailed mineralogical analysis of PM₁₀ fraction leads to the following conclusions:

- a. Mass Concentration of collected dust ranged between 2.5µg/m³ and 79.6µg/m³.
- b. The majority of metal bearing dust grains are metallic minerals that exist in the ore. A mineralogical study of dust settled on filters in the air sampler operating close to the processing facility did not demonstrate variation in the type of metallic minerals. Galena, sphalerite and pyrite dominate, whereas bournotite, boulangerite, chalcopyrite, cerussite, barite, gypsum, goethite and tennantite are subordinate mineral phases. During time periods when winds are of an E-NE direction it seems that seawater droplets are settled on the filters and halite is formed.
- c. The annual limit value PM₁₀ in all stations, as well as the Pb values are lower than the limits permitted by European Standards (40µg/m³ and 0.5µg/m³ respectively).
- d. The number of exceedance days, that is the number of days when Mass Concentration exceeds the daily limit value of 50µg/m³, is significantly lower than the number permitted by European Standards (35 days)². It is worth mentioning that even at the station which is located very close to the processing facilities that number reached a value to 19 during the year 2008.
- e. On the basis of the EU Commission “Thematic Strategy on Air Pollution” published in 2005 the PM₁₀ data at Stratoni pose no risk for human health. However, further research is needed before concluding on the safety of ambient air for the local population. To that end, examination of finer fractions of particulate matter (e.g. PM_{2.5}) as well as collection of data from additional air samplers located within the area of the village of Stratoni is proposed.

² Consultation status in the EU on particulates provisions of the Air Quality Directive (from Goergen & Lambrecht, 2007).

	Commission proposal (09-09-05)	EP first reading (26-09-06)
Limit values for PM ₁₀	a. Daily limit value from 2005 of 50µg/m ³ , which may be exceeded on a max. of 35 days b. Annual limit value from 2005 of 40 µg/m ³	a. Daily limit value from 2005 of 50µg/m ³ , which may be exceeded on a max. of 35 days, but possibility for member States to increase the number of exceedance days to 55 from 2010 b. Annual limit value from 2005 of 40 µg/m ³ in the period from 2005-2010 c. Annual limit value of 33 µg/m ³ from 2010

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7. References

- Argyraki, A., Plakaki, A., Godelitsas, A., 2007. Characterization of garden soil pollution in the mining vil-
lage of Stratoni, N. Greece. *Bull. Geol. Soc. Greece*, 40, 1331-1342.
- Ballas, D. and Gazea, V., 2009. Measurements of PM₁₀ in the area of Stratoni. Unpublished technical re-
port, February 2009, Eurotechnica EPE, Chalkidiki, Greece.
- Cooper, C.D., Alley, F.C., 2004. Air Pollution Control, A Design Approach, 3rd edition, Waveland Press
Inc., 739p.
- DIRECTIVE 2008/50/EC of the European Parliament and of the Council of May 2008 on Ambient air
quality and cleaner air for Europe. *Official Journal of the European Union*, 11-6-2008, L152/1-44.
- Gaidajis, G., 2003. Ambient Concentrations of Total Suspended Particulate Matter and Its Elemental Con-
stituents at the Wider Area of the Mining Facilities of TVX Hellas in Chalkidiki, Greece. *Journal of
Environmental Science and Health*, A38, 10, 2509-2520.
- Gilg, H.A., 1993. Geochronology (K-Ar), fluid inclusion, and stable isotope (C, H, O) studies of skarn,
porphyry copper, and carbonate – hosted Pb – Zn (Ag, Au) replacement deposits in the Kassandra min-
ing district (Eastern Chalkidiki, Greece). PhD Thesis, ETHZ, Zurich, 153p.
- Gilg, H.A., Frei, R., 1994. Chronology of magmatism and mineralization in the Kassandra mining area,
Greece: The potentials and limitations of dating hydrothermal illites, *Geochemica et Cosmochimica
Acta*, 58, 9, 2107-2122.
- Goergen, R., Lambrecht, U., 2007. Particulate Matter in Ambient Air. *Journal for European Environ-
mental & Planning Law*, 4, 4, 278-288.
- Kockel, F., Mollat H., Walther H. W., 1977. Erläuterungen zur Geologischen Karte der Chalkidiki und an-
grenzender Gebiete 1:100.000 (Nord- Griechenland). Hannover, Bundesanstalt für Geowissenschaften
und Rohstoffe, 119p.
- Nebel, M., Hutchinson R., Zartman, R., 1991. Metamorphism and polygenesis of the Madem Lakkos
polymetallic sulfides deposit, Chalkidiki, Greece. *Economic Geology*, 86, 81-105.
- Nikolaou, M., 1960. The Stratoni - Olympias granitic intrusion and the associated mineralization. *Ann.
Geol. Pays. Hellen.*, 2, 214-265.
- Nikolaou, S., 2007. Spatial distribution of potentially toxic elements in soils at NE Chalkidiki, N. Greece.
MSc Thesis, Department of Economic Geology & Geochemistry, University of Athens, Athens, 168
p. (in Greek with English Abstract).
- Papastamatiou, D., 2009. Inhalable particulate matter PM₁₀ in mining areas: The case of Stratoni,
Chalkidiki, Greece. MSc Thesis, Department of Economic Geology & Geochemistry, University of
Athens, Athens, 142p. (in Greek with English Abstract).
- Plakaki, A., 2006. Mobility of potentially toxic elements in soils of the Stratoni mining area, Chalkidiki,
N. Greece. MSc Thesis, Department of Economic Geology & Geochemistry, University of Athens,
Athens, 150 p. (in Greek with English Abstract).
- Plumlee G., Morman, S., Ziegler, T., 2006. The Toxicological Geochemistry of Earth Materials: An
Overview of Processes and the Interdisciplinary Methods Used to Understand them. *In: Sahai, N. &*

- Schoonen, M.A.A. (eds) Medical Mineralogy and Geochemistry*. Mineralogical Society of America, *Reviews in Mineralogy & Geochemistry*, 64, 5-57.
- Posfai, M., Molnar, A., 2000. Aerosol particles in the troposphere: A mineralogical introduction. *In: Vaughan, D.J. & Wogelius, R.A. (eds)*. EMU Notes in Mineralogy, 2, Eoetvos University Press, Budapest, 197-252.
- Skarpelis, N., Argyraki, A., Grypioti, A., 2009. Characterization of sources of inhalable particulate matter (PM₁₀) in the old processing and smelting site of lavrion, Greece. Goldschmidt 2009, Davos, Switzerland, *Special Supplement Geoch. et Cosmoch. Acta* 73, no 13S, p. A 1324.
- Triantafyllou, A., 2000. Patterns and concentrations of PM₁₀ in a Mountainous Basin Region. *Journal of the Air & Waste Management Association*, 50, 1017-1022.
- Triantafyllou, A., Filippidis, A., Patra, A., Pavlidis, A., Kantiranis, N., 2000. Concentrations, mineralogy and morphology of the suspended particles PM₁₀ in the city of Kozani. Proceedings 1st Congress of the Committee of Economic Geology, Mineralogy and Geochemistry, Geological Society of Greece (Kozani), 452-462 (In Greek with English Abstract).

