An Investigation on Heavy Metals in an Industrial Area in Greece

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ABSTRACT: In the industrial area of Elefsis, Greece, aerosol samples from the atmosphere were collected using a stacked filter unit sampler, which separates the airborne particulate matter into coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) size fractions. The samples collected during the period January 2005 to March 2006, were analyzed by anodic stripping voltammetry (ASV) and inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine the fine and coarse particulate concentrations of the heavy metals Zn, Pb, Cd, Cu, Fe, Mn and Ni. Concerning the elements Pb, Cd and Ni regulated by the European Union, annual average concentrations were lower than the prospective assessment thresholds, while concentration levels of Mn were in compliance with the values proposed by the World Health Organization. The concentrations of PM_{10} particulates were about two times as that of the $PM_{2.5}$ particulates. Additionally, the ratio of fine ($PM_{2.5}$) to coarse ($PM_{2.5-10}$) particle concentrations was 0.44, indicating enrichment in the coarse particulates. Fe and Zn concentrations were mostly in the coarse particulate mode. Furthermore, the Pb/Cd average ratio in coarse and fine airborne particulates suggests that Pb is emitted by car exhausts and mainly industrial sources. Moreover, correlation analysis between airborne particulate matter (PM) and toxic elements was carried out to investigate the sources that affect the presence of these elements in coarse and fine particulates.

Key words: Gent stacked, PM_{10}, $PM_{2.5}$, Trace metals, Correlation analysis

INTRODUCTION

Atmospheric aerosol particles play an important role in our everyday life and in the control of different processes in the air (Preining, 1996). Many epidemiological studies have revealed consistent associations between ambient concentrations of inhalable (PM_{10}) and respirable ($PM_{2.5}$) particles with increased mortality, morbidity and decreased lung function (Costa and Dreher, 1997; Saskia *et al.,* 1998; Martuzzi *et al.,* 2003). Although particle size and particle number are considered closely associated to adverse health outcomes, it would be fallible to underestimate the importance of the chemical composition of particles and especially of their content in toxic substances (Harrison *et al.,* 2000; Nabi Bidhendi *et al.,* 2007). Additionally, long-time exposure to toxic trace metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc even at low concentrations can be deleterious to human health (Swielticki *et al.,* 1996; Akoto *et al.,* 2008). The European Union has set an air quality standard for Pb, setting an annual limit value of 0.5 ìg/m³, to be achieved by 2005. Also, the

directive 2004/107/EC proposed as mean annual concentrations for Cd and Ni to be 5 ng/m³ and 20 ng/m³, respectively.

Elevated concentrations of lead can induce severe neurological and haematological effects to the exposed population and especially children. Also, lead affects the metabolism and accumulates in the living tissue. The main source of lead in the atmosphere for many years has been the use of leaded gasoline in vehicles. It is well documented that the use of Pb-containing, anti-knocking gasoline additives had been playing a dominant role in the build up of atmospheric Pb levels (Simpson *et al.,* 1994; Dixit *et al.,* 2008). Since the lead content in fuels has been regulated during the past years, smelter processes, fuel burning activities and other industrial sources contribute in the ambient lead production (EC, 1997).

Compounds of cadmium and nickel are susceptible for inducing carcinogenic effects in human, through inhalation. Cadmium is a toxic metal for most living species, and it is emitted by electroplating and battery

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production industries. Furthermore, cadmium and nickel compounds in particulate matter mainly originate from coal and fuel oil combustion processes, metallurgical industry and road transport (EC, 2001; Mugica *et al.,* 2002). Nickel is one of the metals used in the electroplating industry. Continuous and prolonged exposure to nickel can produce dermatitis and disorders in the respiratory system. Ni-bearing particles occur in the atmosphere as part of suspended particulate matter and, rarely, of mist aerosols. Ni is commonly associated with the fine particulate matter fraction of ambient air samples with diameters ranging from 0.6 to 10 ìm. Iron and manganese are related to industrial processes. Manganese is a neurotoxic element that in continuous and prolonged exposure causes a neurological disease called manganism. Concerning manganese, exposure to increased levels is known to lead to neurotoxical impairments. The suspension of crustal particles (Harrison et al., 2003) and industrial activities are possibly responsible for the ejection of manganese in the atmosphere. Iron is a potentially toxic element that acts as a catalyst in the development of the highly free oxygen radicals in living organisms (Hemminki et al., 1995). Moreover, elements such as Pb, Cu and Zn are mainly found in the particulate phase. These metals are mostly emitted into the atmosphere by heavy industry, coal burning, metallurgical smelters and automobile traffic (Pacyna, 1986). Zinc is also used in the lubricant additive zinc diethyldithiophosphate and is therefore likely to be incorporated into road dusts through oil leakage, and exhaust particles through oil combustion. A contribution from road traffic for Zn is therefore likely, but is not dominant. Additionally, emissions of atmospheric copper are primarily due to metal production and other industrial processes. The ever-increasing dispersion of heavy metals through the atmosphere, water and soil is a major concern due to their hazardous effect on human health, the possible changes they initiate in natural biochemical processes in all ecosystems and their inevitable accumulation in the food chain.

Up to these days, several studies, on the composition of particulate matter in metals, have been reported for Athens (Scheff *et al.,* 1990; Torfs *et al.,* 1997; Protonotarios et al., 2002; Thomaidis et al., 2003; Manalis et al., 2005) and Thessaloniki, Greece (Samara *et al.,* 1990; Manoli *et al.,* 2002; Voutsa *et al.,* 2002; Samara *et al.,* 2005). In the framework of an environmental study, an ambient particulate monitor (tapered oscillating microbalance - TEOM) (Rupprecht & Patashnick Co, Inc., TEOM Series 1400) was used for the industrial area of Elefsis in order to compare the results found for the PM$_{10}$ airborne particulates with those using a Gent stacked filter unit. The findings showed for the period January 2005 to December 2005

that there was a very good agreement for the PM$_{10}$ concentrations, 67.0±55.4 ìg/m^3 (TEOM) and 69.0±21.8 ìg/m^3 (Gent-stacked filter unit), respectively. The objectives of this investigation include characterizing fine (PM$_{2.5}$), coarse (PM$_{2.5-10}$) and inhalable (PM$_{10}$) concentrations and atmospheric heavy metals, and studying their temporal variations taking into account the meteorological parameters. Correlations between coarse (PM$_{2.5-10}$), fine (PM$_{2.5}$) particulates and heavy metals have been extracted to identify the major source types in the industrial area of Elefsis, Greece.

MATERIALS & METHODS

Size fractionated airborne particulates were collected by means of a Gent-type stacked filter unit (Maenhaut *et al.,* 1994; Hopke *et al.,* 1997; Hien *et al.,* 2002; Salma *et al.,* 2006, Kothai *et al.,* 2009), during the period from January 2005 to March 2006, at an industrial area, Elefsis/Greece.

The sampling station belongs to the Bureau of Pollution and Environmental Quality Control of the Development Association of Thriassion Plain, Elefsina, and is close to the old and narrow exit road from Athens to Corinth. The major industrial plants in the greater industrial zone that affect the sampling site include two oil refineries, two cement manufacturing plants, two shipyards and a steelworks factory (Fig. 1).

The sampler was installed at a height of 3 m above ground level and the flow rate of sampling was 16.7 L/min. The operation time for sampling was midnight-to-midnight. The separation of the aerosol particles into two size fractions was achieved by the sequential filtration through two Nuclepore track-etch polycarbonate filters (Whatman) of different pore size; each filter has a diameter of 47 mm. The first (coarse) and the second (fine) filters were placed in a stacked filter cassette that is equipped with an upper-size inlet cut-off.

Furthermore, the initial filter is an 8 μm pore 47 mm Nuclepore filter and the second filter is an 0.4 μm pore Nuclepore filter. The Gent sampler allows the collection of coarse particles with Effective Cut off Diameter (EAD) between 10 and 2.5 μm (PM$_{10}$) in the first stage and fine particles with EAD 2.5 μm (PM$_{2.5}$) in the second stage. As preliminary studies had shown that the amount of aerosol sampled within 24 h in that area was often less than 1 mg, the duration of each sampling period was prolonged to 48 h starting at midnight, to collect enough airborne material for the analyses.

For the leaching process, HNO$_3$ 65% w/w (Suprapure, Merck), HCl 30% w/w (Suprapure, Merck) were used. High purity water (HP water) was obtained from a Water Purification System (Barnstead, Easypure RF). Also, for the pH adjustment NH$_3$ 25% w/w
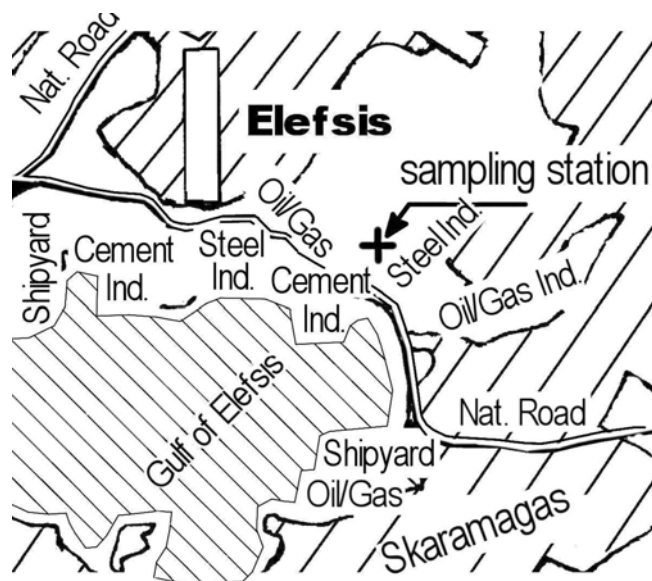
Fig. 1. Map of the Elefsis area with the sampling station and the location of different industries

(Suprapure, Fluka Chemika) was used as well as 0.1 N HCl, produced from HCl suprapure and high purity water (HP water). Bromophenol blue, 0,05% in HP water was applied as pH indicator (pH: 3.0-4.6). ASV and ICP-AES measurements were carried out by using standard solutions of Zn, Pb, Cd, Cu, Fe, Mn and Ni, each 1000 mgL^{-1} (Fluka), appropriately diluted to 2% HNO$_3$. Anodic stripping voltammetry (ASV) measurements for determining Zn, Pb, Cd and Cu were performed with a 747 VA Stand (Metrohm) connected with a 746 VA Trace Analyzer (Metrohm). The working electrode was a multimode Hg electrode, the reference an Ag/AgCl electrode filled with 3 M KCl in HP water and the auxiliary electrode a Pt-electrode. The measuring parameters were, drop size: 4, time measured: 20 ms, sweep rate: 20 mVs^{-1}, voltage amplitude: 20 mV. The pre-electrolysis time was 180 s with slow stirring at a voltage of -1400 mV. An ULTRAsonik type ultrasonic bath (NEY, 28H) was used for leaching. ICP-AES measurements for the elements Zn (206.200 nm), Pd (220.353 nm), Cu (223.008 nm), Fe (238.204 nm), Mn (260.569 nm), Ni (231.604 nm) were performed with a sequential instrument (Jobin Yvon 138 Ultrace).

Assuming a collected volume of 48 m^3 the detection limits of the chemical analyses were 21 ng/m^3 for Zn, 46 ng/m^3 for Pb, 37 ng/m^3 for Cu, 37 ng/m^3 for Fe, 4 ng/m^3 for Ni and 1 ng/m^3 for Mn using ICP-AES, whereas by using ASV the detection limits were 6 ng/m^3 for Zn, 0.7 ng/m^3 for Pb, 0.4 ng/m^3 for Cd and 0.8 ng/m^3 for Cu, respectively. The metal content of blank sample filters was below detection limits. Nuclepore filters were pre- and post-weighed to determine the gravimetric masses of collected materials using a Mettler balance (Model XS205 DualRange) placed in a dedicated room with controlled temperature and humidity. The readability of the balance is 0.1 mg.

The filters loaded with airborne particulates, were weight (w_1), then by use of plastic scissors about one quarter from the whole filter was cut and was also weight (w_2). That was necessary as the filters were used also for other analytical methods. By the ratio of w_2/w_1 the percentage of the used filter was calculated. The filter sample was now cut into smaller pieces and transferred into an ultrasonic bath. In the ultrasonic extraction procedure, one quarter from a filter loaded with airborne particulate matter or from a blank filter was leached for 30 min with HNO$_3$/HCl. The obtained solution was then diluted to a final volume of 25 ml using HP water and was measured by ICP-AES. From each one of the solutions produced, 4 ml were transferred into a polarographic cell, stirred by a small magnetic stirrer and, after adding 1 drop of bromophenole blue pH indicator solution, the solutions were roughly titrated with NH$_3$ suprapure in a 1st step, until the color change of the indicator. In a 2nd step the solutions were back-titrated with 0.1 N HCl to reverse indicator change region, so that a pH of about 3.0 was assured.

The polarographic cell was then transferred to the polarograph; the solution was de-aerated for 2 min by N$_2$ and analyzed by ASV. The analysis was performed with a hanging mercury drop electrode (HMDE) in the square wave mode. The calculation of the concentration was performed by the standard addition method. For the evaluation and demonstration of the obtained results the programs "Systat 9" (SPSS Inc., Chicago, USA) and "Origin Pro 7.5 SR4, (Origin Lab corporation, Northampton, USA) were used.

RESULTS & DISCUSSION

PM_{10}, $PM_{2.5-10}$ and $PM_{2.5}$ concentrations are given in Fig. 2. The average concentration of the value of 50 μg/m³ (not to be exceeded over 35 times in a year) was 86%. Concerning fine PM there are not yet limit values for the European Union, although the EC has produced the II Position Paper on PM where $PM_{2.5}$ monitoring is recommended and possible limit values are supplied (EC, 2003a). Compared with the recent national ambient air standards for fine particles smaller than 2.5 μm in diameter the annual average limit of 15 μg/m³ (US EPA, 1997) is exceeded. The highest PM_{10} particulate concentrations were observed during April 2005, that can be explained by the fact that calm conditions (wind velocity < 0.5 m/sec) prevailed. Table 1 indicates that the average coarse particulate concentrations were about two Fig.2 PM_{10} particulates exceeded the EU proposed annual limit value of 40 μgm⁻³ (to be achieved by January 2005) (EC, 1999) regarding the sampling site. The percentage of daily PM_{10} concentrations
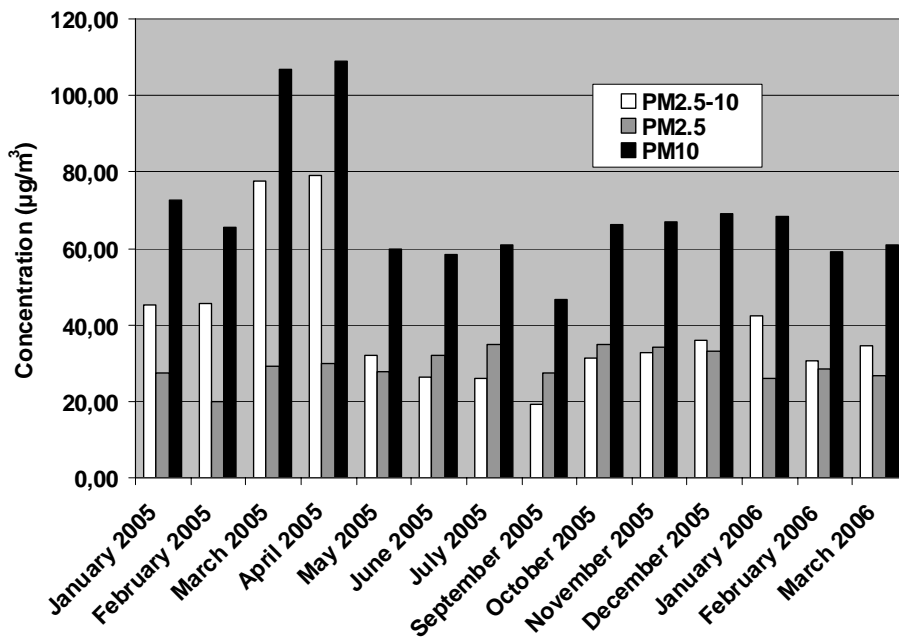

Fig. 2. Seasonal variation of PM_{10}, $PM_{2.5-10}$ and $PM_{2.5}$ concentrations from January 2005 to March 2006

Table 1. Fine, coarse and PM_{10} particulate concentrations; coarse/fine ratios during January 2005 – March 2006 (μg/m³) for the Elefsis area

Month	Fine Particulates ($PM_{2.5}$)	Coarse Particulates ($PM_{2.5-10}$)	PM_{10} Particulates	Ratio $PM_{2.5}/PM_{10}$
January 2005	27.45	45.25	72.70	0.38
February 2005	20.03	45.63	65.66	0.30
March 2005	29.15	77.55	106.70	0.27
April 2005	29.87	78.96	108.83	0.27
May 2005	27.85	31.95	59.80	0.46
June 2005	31.97	26.38	58.35	0.55
July 2005	34.90	26.07	60.97	0.57
August 2005	27.40	19.40	46.80	0.58
September 2005	34.80	31.50	66.30	0.52
October 2005	34.30	32.80	67.10	0.51
November 2005	33.20	35.85	69.05	0.48
December 2005	25.97	42.43	68.40	0.38
January 2006	28.43	30.57	59.00	0.48
February 2006	26.65	34.37	61.02	0.44
March 2006	24.79	41.98	66.77	0.35
Average	29.12	40.05	69.16	0.44
Stdev	4.17	17.17	16.83	0.10

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higher than the 24-h times of fine particulate concentrations except for the months June 2005 to October 2005. Furthermore, the ratio of fine particle concentrations to coarse particle concentrations display that the coarse particle concentrations were almost greater than that of fine particle concentrations, so there is enrichment in the coarse particulates.

Moreover, the monthly ratios of $PM_{2.5}/PM_{10}$ ranged from 0.27 to 0.58. The ratios of fine particle/coarse particle were averaged 0.44. Similar ratios of $PM_{2.5}/PM_{10}$ for other industrial sites were reported for Canada (Cheng *et al.,* 2000) and Beijing (Sun *et al.,* 2004) with values of 0.52 and 0.48, respectively. Particle mass and elemental concentrations in PM_{10} and $PM_{2.5}$ particulates collected in Elefsis during the period January 2005 to

March 2006 are displayed in Table 2. The obtained results show that the mean PM_{10} concentration in Elefsis was 67.7 µg/m³. On the other hand, higher PM_{10} mean concentrations were reported in the industrial area of Thessaloniki, Greece with a mean value of 78 µg/m³ (Voutsa *et al.,* 2002). Furthermore, lower PM_{10} mean concentrations were reported for Athens, Greece during June 2001 to May 2002 with a mean value of 54.9 µg/m³ (Manalis *et al.,* 2005).

Regarding lead concentrations, the annual limit value of 500 ng/m³, is higher than the measured Pb concentration at Elefsis. The recent directive of the European Parliament and of the Council relating to arsenic, cadmium, mercury and polycyclic hydrocarbons in ambient air sets assessment

Table 2. Particle mass and elemental concentrations in PM_{10} and $PM_{2.5}$ in industrial regions of Greece

	Present study		Christidis 1988-1990	Greece 1997-1998	Greece 2001-2002
	PM_{10}	$PM_{2.5}$	TSP	Thessaloniki, PM_{10}	Athens, PM_{10}
PM	67.7±20.7 (N=49)	29.5±6.9 (N=49)	145±55 (1988) 154±60 (1989) 158±57 (1990)	78	54.9±28.3
Zn	938±913 (N=49)	474±696 (N=49)	544±476 (1988) 736±613 (1989) 1260±946 (1990)	218	-
Pb	322±217 (N=49)	146±162 (N=49)	313±200 (1988) 482±253 (1989) 368±262 (1990)	206	71.1±47.9
Cd	3.25±2.90 (N=49)	1.62±2.70 (N=49)	3.5±2.9 (1988) 3.1±3.8 (1989) 10.3±14.2 (1990)	1.3	3.7±2.4
Cu	123±76 (N=49)	50±31 (N=49)	120±35 (1988) 184±110 (1989) 592±493 (1990)	36	43.2±32.6
Fe	1503±1163 (N=49)	621±946 (N=49)	4617±2591 (1988) 4417±2184 (1989) 5209±2241 (1990)	1760	-
Mn	93±93 (N=45)	47±65 (N=45)	179±128 (1988) 216±140 (1989) 253±150 (1990)	65	21.1±19.4
Ni	18±10 (N=32)	9±6 (N=32)	30±19 (1988) 29±13 (1989) 19±7 (1990)	11	15.9±8.3

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thresholds for As, Cd and Ni. The mean annual concentration proposed for As is 6 ng/m^3, 20 ng/m^3 for Ni and 5 ng/m^3 for Cd (EC, 2004). Mean concentrations of Cd and Ni are lower than the respective assessment thresholds at the industrial area of Elefsis. Additionally, in the Air Quality Guidelines of 2000 WHO includes an annual tolerance concentration of 150 ng/m^3 for Mn, which is higher than the observed concentration.

On the other hand, Zn could be released from tires due to the friction and heating and is also used as a pesticide component. The total contribution of these sources, including industrial sources, made the Zn mean value reach 938 ng/m^3 in the PM$_{10}$ particulates. High concentrations for Zn were also reported for an industrial site in Thessaloniki, Greece (Voutsa et al., 2002). Mn, also related to industrial processes and brake-drum abrasion (Harrison et al., 1996) was detected at mean value of 93 ng/m^3 in the coarse particulates. Concerning Cu, one of the heavy metals characterized by its toxicity, it showed a mean value of 123 ng/m^3. With regard to Ni, this element is mainly associated with fossil fuel use, oil burning and emissions from stationary and industrial sources. This compound had a mean value of 18 ng/m^3. The values found for Zn, Pb, Mn and Cu were higher than those reported in the literature for Thessaloniki, Greece (Manoli et al., 2002) and Athens, Greece (Manalis et al., 2005) that can be explained due to the fact that the sampling site is close to a number of industries including cement and steel industries, oil refineries. Ni and Cd concentrations for the PM$_{10}$ particulates given by Manalis et al. were similar with those shown in Table 2 for the investigated area. It is worth pointing out that Fe concentrations were close to the values found by Voutsa et al. for the industrial area of Thessaloniki. Levels of heavy metals were also similar to those given by Kim et al. (2002) in moderately polluted areas (Taejon, Korea; Oporto, Portugal). However, if we compare the results obtained for the heavy metals Cu, Fe and Mn for the same sampling site (Elefsis) with those found in the period 1988-1990 (Christides, 1995) the values have substantially decreased, indicating smaller industrial activity. Finally, the Pb/Cd average ratios were calculated for the PM$_{10}$ and PM$_{2.5}$ particulates for the investigated sampling site in order to show the direct anthropogenic contribution for the industrial area. The Pb/Cd ratios for the two particulate size fractions were 99 and 88, respectively. Similar ratios for Pb/Cd in an industrial site influenced by heavy road traffic were reported by other authors (Moreno-Grau et al., 2000). Comparing Pb/Cd ratios from Elefsis with those values reported for global natural emissions (mean Pb/Cd of 40) (Nriagu et al., 1988) the significance of anthropogenic contribution to the total burden of toxic metals in PM$_{10}$ and PM$_{2.5}$ particles is obvious.

Figs. 3-6 show, for the sampling area of Elefsis, the temporal variations of metals in the investigated area. Pb was observed to have higher concentrations in the PM$_{10}$ particulates during the winter period (January 2005 - February 2005) where the annual limit of 0.5 µg/m^3 was exceeded. Furthermore, Ni was below the threshold limit value of 20 ng/m^3 in both PM$_{10}$ and PM$_{2.5}$ airborne particulates. Higher concentrations of Ni were observed during the period December 2005 - January 2006, indicating the impact of large scale industrial activity characterizing the investigated area. Moreover, the concentrations for the elements Fe, Zn, Pb, Cu and Ni were lower in PM$_{10}$ and PM$_{2.5}$ particulates during the summer period (June 2005 - August 2005) compared with the winter period, suggesting less influence from the industries that exist near the sampling area. In Athens, Greece, atmospheric particulate Pb and Ni were observed in higher concentrations during winter (Thomaidis et al., 2003). Correlation coefficients were obtained for each metal against the other metals and PM in coarse and fine particulates for summer and winter period (Table 3).

average concentrations for PM$_{10}$ and PM$_{2.5}$ particulates, respectively. The elements Fe and Zn were in higher proportions in the PM$_{10}$ and PM$_{2.5}$ particulate fractions compared with the other elements PM concentrations were not strongly correlated to any one of the metals in both coarse and fine particulates for both summer and winter, presumably due to the large number of emissions sources of different types located around the station. Strong correlations were found between the elements Zn/Pb, Zn/Cu and Zn/Fe, Pb/Cu and Pb/Fe, Cu/Fe and Fe/Mn in the coarse airborne particulates for the summer period that can be associated with traffic, industrial sources and road dust. For the winter period, Fe was well correlated with Mn in coarse particulates. On the other hand, Zn showed a significant correlation with Fe while Cu correlated with Mn but not strongly in fine particulates during summer period. Furthermore, Zn correlated with Pb, Fe in fine particulates in winter period. Moreover, it must be mentioned that if we compare the correlation coefficients obtained for both coarse and fine airborne particulates for summer and winter period, PM concentrations at the sampling site did not show strong correlations with any of the metals measured in this study. Additionally, coarse particulates compared with fine particulates in the summer period were significantly correlated with the investigated metals. Fe was well correlated with Mn in coarse particulates in summer and winter period in comparison with fine particulates. As a conclusion, the above metals are emitted from various industrial activities taking place in the sampling area (oil refineries, iron and steel industry, shipyards).
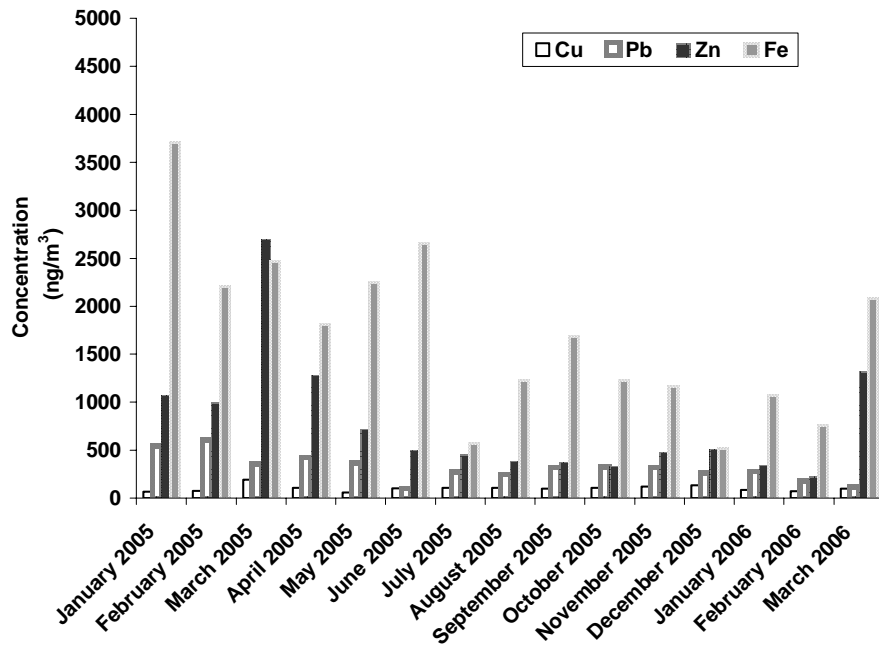
Fig. 3a. Temporal variations of Cu, Pb, Zn, Fe average concentrations in PM$_{10}$ particulates in the industrial area of Elefsis
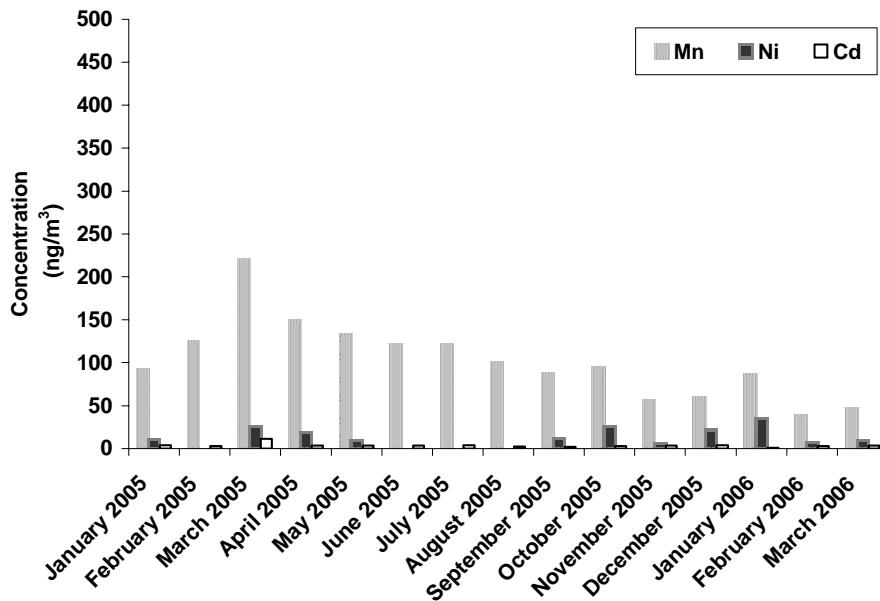

Fig. 3b. Temporal variations of Mn, Ni, Cd average concentrations in PM$_{10}$ particulates in the industrial area of Elefsis

CONCLUSION

In the present study the concentrations of Zn, Pb, Cd, Cu, Fe, Mn and Ni in PM$_{2.5-10}$ and PM$_{2.5}$ particles were measured using low volume Gent stacked filter unit in an industrial area in Greece, during the period January 2005 - March 2006. The average concentrations of the PM$_{10}$ particulates exceeded the EU proposed annual limit value of 40 μgm^{-3} (to be achieved by January 2005) regarding the sampling site. Also, the ratios of fine particle/ coarse particle were averaged 0.44, indicating that there is enrichment in coarse particulates. Furthermore, the concentrations for the elements Pb, Cd and Ni regulated by the European Union were lower than the prospective assessment thresholds, while concentration levels of Mn were in compliance
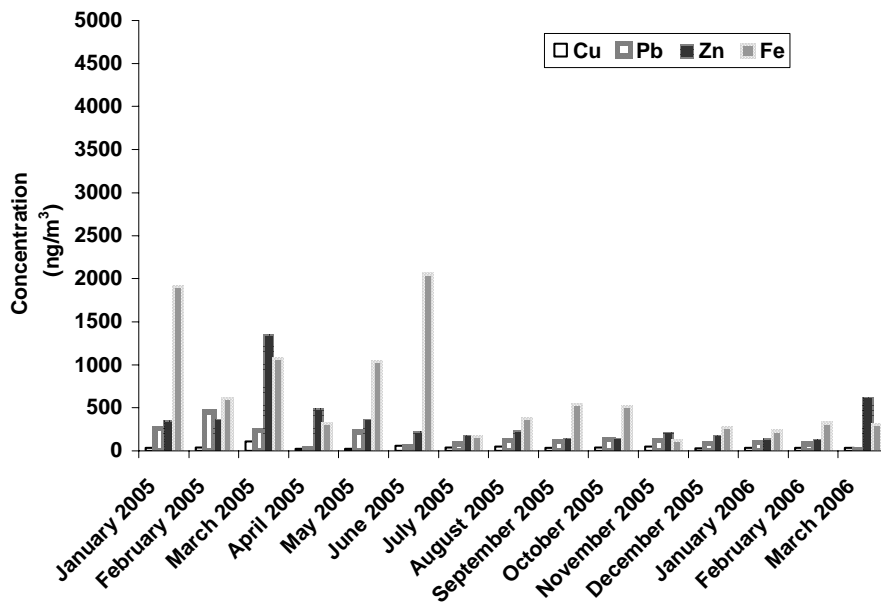
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Fig. 4a. Temporal variations of Cu, Pb, Zn, Fe average concentrations in PM$_{2.5}$ particulates in the industrial area of Elefsis
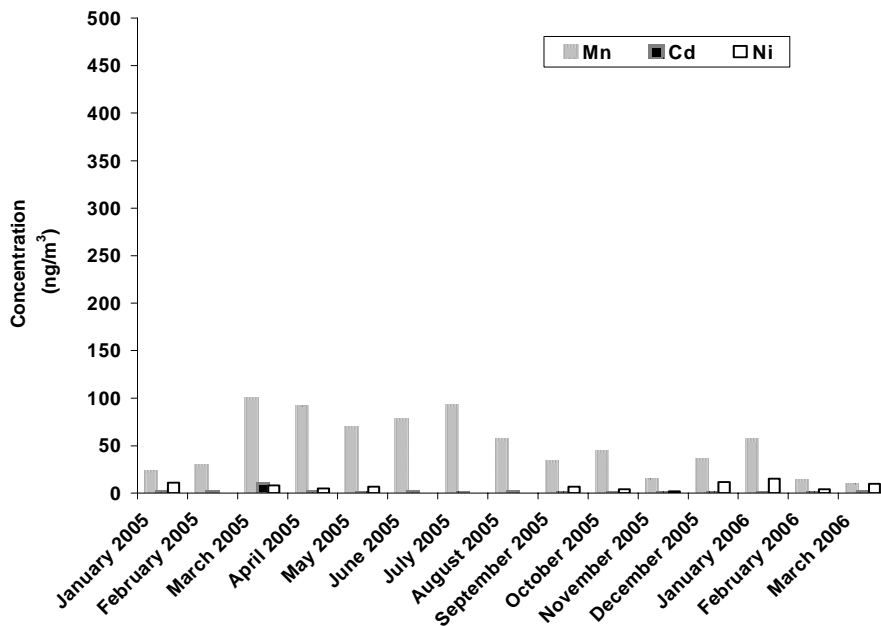

Fig. 4b. Temporal variations of Mn, Ni, Cd average concentrations in PM$_{2.5}$ particulates in the industrial area of Elefsis

with the values proposed by the World Health Organization. The Pb/Cd ratios found for the PM$_{10}$ (PM$_{2.5-10}$ + PM$_{2.5}$) and PM$_{2.5}$ particulates were 99 and 88, respectively. Finally, correlation analysis was carried out in order to identify individual emission sources in the coarse (PM$_{2.5-10}$) and fine (PM$_{2.5}$) particulate size fractions.

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Table 3. Correlation analysis of metallic elements and PM in Elefsis, Greece: a) coarse particulates (summer period), b) coarse particulates (winter period), c) fine particulates (summer period) and d) fine particulates (winter period)

(a)	PM	Zn	Pb	Cu	Fe	Mn	Ni
PM		1.000					
Zn	-0.084	1.000					
Pb	-0.257	0.931	1.000				
Cu	0.030	0.878	0.786	1.000			
Fe	-0.102	0.799	0.769	0.825	1.000		
Mn	-0.299	0.513	0.549	0.582	0.707	1.000	
Ni	0.293	-0.064	-0.073	0.088	-0.050	0.026	1.000
(b)							
PM	1.000						
Zn	0.388	1.000					
Pb	0.021	0.261	1.000				
Cu	-0.193	-0.089	0.207	1.000			
Fe	0.205	0.178	0.203	-0.150	1.000		
Mn	0.093	0.195	0.278	-0.022	0.742	1.000	
Ni	0.154	0.513	0.081	-0.246	0.192	0.197	1.000
(c)							
PM	1.000						
Zn	-0.000	1.000					
Pb	-0.022	0.010	1.000				
Cu	0.056	0.338	0.086	1.000			
Fe	0.079	0.838	-0.316	0.473	1.000		
Mn	0.452	0.397	0.421	0.562	0.401	1.000	
Ni	0.100	0.133	0.132	-0.017	0.136	0.438	1.000
(d)							
PM	1.000						
Zn	-0.428	1.000					
Pb	-0.031	0.570	1.000				
Cu	-0.036	0.087	0.081	1.000			
Fe	-0.275	0.526	0.115	0.110	1.000		
Mn	-0.075	0.305	0.187	0.399	0.431	1.000	
Ni	0.383	-0.218	-0.105	-0.397	0.092	0.121	1.000

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