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Estimation of selected heavy metals and arsenic in PM_{10} aerosols in the ambient air of the Greater Athens Area, Greece

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Abstract

Aerosol samples of PM_{10} were collected during summer and winter 2003 at two different sites in the Messogia Basin northeast of Athens, to demonstrate the variations of heavy metals in PM_{10} and examine their relationship with both gaseous pollutants and meteorological parameters. Estimated heavy metals during the experimental campaign were mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni) and arsenic (As). The average heavy metal concentrations for the first site (Spata) constituted 0.66–14.7 ng/m^3 for the summer period and 0.14–19.5 ng/m^3 for the winter period. At the second site (Koropi), the corresponding values varied between 0.89 and 13.3 ng/m^3 and 0.16 and 24.7 ng/m^3, respectively. PM_{10} Hg, PM_{10} Cd and PM_{10} Ni contents showed regular daily variations, with higher mass percentages during the summer, indicating differences in local PM_{10} sources for each season. On the contrary, PM_{10} Pb presented higher mass percentages during the winter. Examination of the relationship between heavy metals and meteorological parameters indicated a higher correlation with temperature and relative humidity, especially for Pb. In addition, most of the heavy metals (apart from Hg) presented an expected correlation with nitrate oxides (NO_x), PM_{10} and ozone (O_3). Higher correlations with both meteorological parameters and gaseous pollutants were observed during the winter experimental campaign. Maximum heavy metal concentrations at both sites were observed during days with NE or NNE prevailing winds during the summer campaign, while the winter period was characterized with maximums during days with W or WNW prevailing winds.

Keywords: Heavy metals; PM_{10} percentage; Meteorology; Gaseous pollutants

1. Introduction

Atmospheric particulate matter (PM) in urban areas has many sources, the majority of which are closely related to human activity. Heavy metals emissions from factories or car exhausts can result in serious environmental problems such as the restriction of atmospheric visibility, while their toxicity may present health problems to humans at certain concentrations [1]. Furthermore, these pollutants, with their high potential toxicity, affect soil processes and lead to the degradation of soil conditions. As a result, plant toxicity is raised and the entry of contaminants into the food chain is inevitable. For example, the As transportation and detoxification in "*Escherichia coli*" and "*Saccharomyces cerevisiae*" has been examined in the past [2]. In both species As is taken up by phosphate transporters, and aquaglyceroporins GlpF and Fps1p facilitate As entry into cells. The first step in arsenate detoxification is biotransformation to As by an arsenite reductase, ArsC or Acr2p. In both organisms, the next step involves extrusion of As from the cytosol. Coli extrusion is catalyzed by the ArsAB ATPase. In yeast this is carried out by the arsenite carrier, Acr3p. In addition, Ycf1p, a homologue of the human MRP drug pump, transports glutathione conjugates of As into the yeast vacuole [2].

Airborne aerosols' chemical and physical compositions vary depending on location, season and local meteorology [3,4]. Hg is a volatile metal, which occurs in the atmosphere as gaseous

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compound and in the particulate phase [5–8]. It is among the most highly bio-concentrated trace metals in the human food chain and this is the reason why several international committees have already targeted Hg for special attention, giving specific guidelines for their emissions, cycling and health affects (WHO, US-EPA).

Metallic Hg has been proved to be of great danger for the human nervous system, kidneys and skin [9]. Thus, safety limits have been established, implying that Hg vapour should not exceed 0.1 mg/m^3 in ambient air [10] since almost 80% of inhaled Hg is stored in human body [11]. Additionally, Hg is a very volatile element with a high vapour pressure at room temperature. Thus, dangerous levels can easily be obtained in indoor environments. Refuse incineration of fluorescent lights, batteries, electrical switches, thermometers and general waste [12] is the main source of Hg in the air. The airborne emissions from such incineration contain major fractions of particulate mass of <1 μm [13]. In that case, these particles usually play a significant role in the transportation of Hg over long distances, since particles between 0.1 and 1 μm have relatively long atmospheric residence times [14].

Coal-fuelled power plants and copper and Pb smelters are the largest point sources of As in the air [15]. Pesticides, fungicides, weed killers and wood treatment products release As into the environment. These releases are primarily related to soil, air and water. Although As does form organic gaseous species when burnt, it is mainly present in the fine particle phase [16,17] and the burning of fossil fuels is the main source. The burning of treated wood is of particular concern, as the smoke may contain dangerous amounts of As compounds [18] and other chemicals used to treat the wood (such as chromium and copper compounds). Epidemiological studies have demonstrated that a long-term exposure to inorganic As is associated with an increased risk of cancer of the skin, lungs and other body sites [19,20].

On a global basis, anthropogenic inputs of Pb predominate over natural sources, accounting for 96% of the total emissions [21]. Among these inputs, vehicular and roadside emissions of particles are often found to be the most significant sources. It is also well known that the use of Pb containing, anti-knocking gasoline additives play a significant role in the rise of atmospheric Pb levels globally [22]. Residence time of these particles is of the order of days and can be affected by the frequency and amount of rainfall [23]. Thus, Pb can influence areas, which are far from the emission point. Despite the fact that Pb-free petrol has become a common choice for most transport facilities, Pb is still found to be an important component of airborne particles throughout the world [24]. The association of Pb with vehicular emissions can be explained in terms of Pb contamination in crude oil, which may be of the order of 10–15 mg/l [25]. The European Commission has adopted a Proposal for a Directive, which set, for the first time, European Union (EU) limit value for Pb in the air we breathe. The proposal's major goals are to provide a high level of protection for public health across the EU and to improve the quality of life for European citizens. The limit value for Pb is 0.5 μg/m^3, to be met on 1 January 2005.

A large number of studies have been conducted around the world, to demonstrate the variations and characteristics of heavy metals in both local and peripheral level. In particular, mean Hg and As concentrations reported for southern Taiwan, reached values of 2.63 and 5.99 ng/m^3, respectively [26]. Corresponding values have been reported for Pb (118 ng/m^3) in Madrid [27] and for Ni (0.83 ng/m^3) and Pb (18.7 ng/m^3) in Saragosa [28]. Finally, the chemical characterization of PM_{10} at an urban, a suburban and a rural site in Switzerland, presented differences in Ni, As, Cd and Pb concentrations, related to the prevailing sources in all stations, since the corresponding values were 3.0, 0.8, 0.26 and 49 ng/m^3 for the city centre, 3.6, 0.68, 0,26 and 50 ng/m^3 for the suburbs and 1.8, 0.44, 0.23 and 20 ng/m^3 for the rural area [29].

Studies concerning heavy metal levels in PM in Greece have already been reported [30–32]. Little work, especially for the Greater Athens Area, has been carried out as far as PM are concerned. In particular, Koliadima et al. [33] studied the size and distribution of Pb, Zn, Cu, Cr and Mn in atmospheric particles during 1992, while Siskos et al. [34] reported the first systematic work for chemical characterization of $PM_{2.5}$ aerosols concerning acidity and major cations and anions, during a 1-year period (1995–1996).

It is the purpose of this work to demonstrate the variations of heavy metals in PM_{10} and examine their relationship with both gaseous pollutants and meteorological parameters, in the Greater Athens Area. Additionally, an attempt to recognize the emission rates as well as the transportation of heavy metals is performed.

2. Materials and methods

2.1. Site description

The experimental campaign took place at two sites (see Fig. 1) located in the vicinity of the Messogia Basin, northeast of Athens. The Messogia Basin is separated from Athens by the mountains of Ymettus (1026 m) and Pendeli (1107 m). Land use has been predominantly agricultural in nature, but has changed significantly in recent decades, particularly with the construction of a highway (Attiki Odos) connecting the region with the city centre, the new Athens International Airport (AIA) and other industrial and housing development [35]. The first site was located on the flat area of the Health Centre of the town of Koropi, 5 km southwest of the AIA, on the foot of Ymettus Mountain. This mountain plays a significant role in local air pollution levels, since it separates the area from the city of Athens and allows Koropi to maintain its local circulation characteristics. Concerning the town of Koropi itself, it combines both agricultural and urban characteristics. Busy road crossings contribute to pollution levels higher than background levels, while intense agricultural activity is a source of additional emissions, especially due to wood burning during the winter period. The town population is approximately 10,000, while the buildings are mainly detached with two or three floors each. Finally, a solid waste treatment facility (SWTF) located in the west-northwest of the sampling site of Koropi, appears to play a significant role

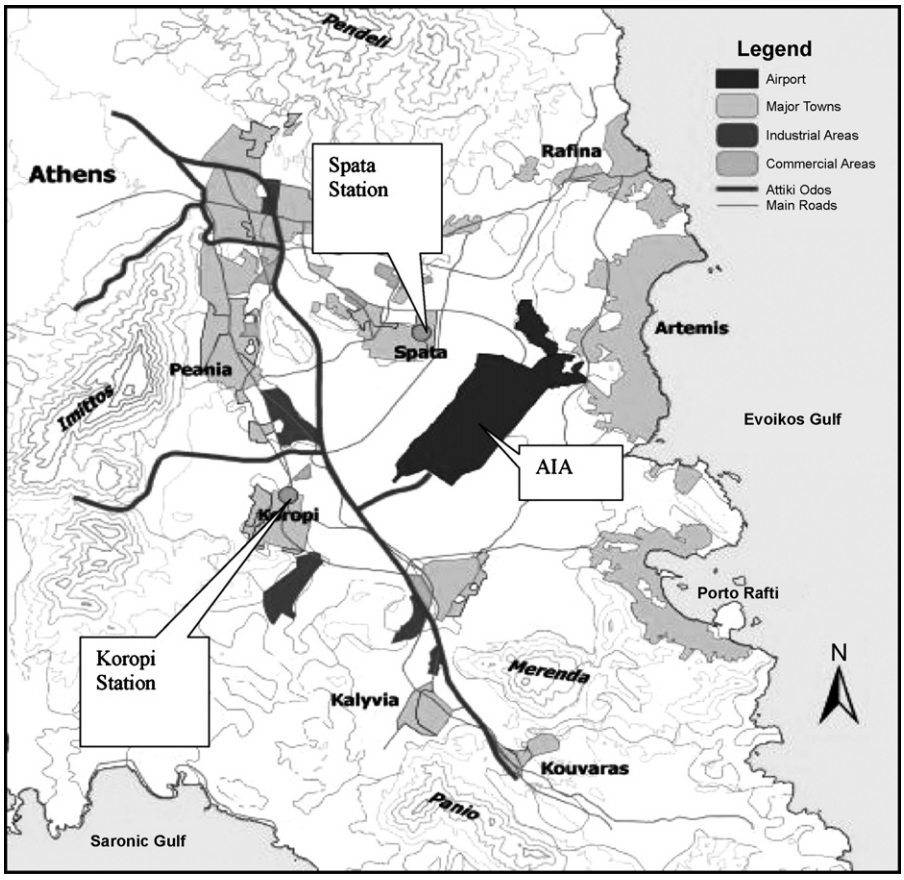

Fig. 1. Map of the Greater Messogia Area, where both the experimental sites are shown. The Athens International Airport as well as the Attiki Odos are clearly illustrated.

in the pollution levels of the region. This area was used for the burning of residential waste years before the experimental campaign, but still consist a significant pollution source for Koropi region.

The second sampling location is sited on the bypass road of the Health Centre of the town of Spata (see Fig. 1), 3 km northwest of the AIA. Spata's local characteristics are slightly different than those of Koropi since agricultural activity is not as prevalent, while local vehicular traffic is much more intense than in Koropi. In particular, the monitoring site lies near crossroads with traffic lights, where vehicular emissions are enhanced. Building constructing works taking place in close proximity with the sampling site during the experimental campaign is an additional factor influencing the pollution levels.

The mean wind pattern in the atmospheric boundary layer in the vicinity of the Messogia region can be characterised by a predominantly northeastern flow. The area is exposed to the summer monsoon circulation driven by the Arabian heat low. The resulting northern winds in the Aegean, are occasionally interrupted by the passage of weak pressure troughs [36,37]. In this case, the surface wind flow at Koropi is a combined result between the Evoikos and the Saronic Gulf sea breeze cells, where in most cases the first is reaching the Koropi area and the second is blocking the southern passage of Messogia Plain [38]. Corresponding phenomenon may appear in Spata, where the surface wind flow is influenced by the Evoikos Gulf sea breeze blowing from the E to NE directions, depending on the background flow [39]. Finally, under low background flow during the night, the Koropi area is under the influence of the Ymettus katabatic flow (NW-W flow), while the Spata area is influenced by the western land breeze flow. During the daytime anabatic winds are more evident at the Koropi area.

2.2. Instrumentation and sampling

The first sampling campaign was conducted in June 2003 (between 4th and 17th) in order to cover the summer period. Hourly averaged nitrate oxide (NO), nitrate dioxide (NO_2), and O_3 measurements were provided by the Environmental Department of the AIA, which operates air quality monitoring stations at the two sites (Spata and Koropi) supervised by the Hellenic Ministry for the Environment, Physical Planning and Public Works. PM_{10} values were recorded on a 24-h basis, while hourly averaged meteorological data, concerning the wind speed, wind direction, temperature and relative humidity, collected with 10-m masts were also available.

The second sampling campaign was held in November 2003 (between 11th and 29th), presenting different meteorological conditions than the first campaign. Atmospheric samples were collected from the same sites using the same sampling procedure as in the first experimental campaign.

The available instrumentation for both experimental periods and both sites consisted of: Horiba APNA 360 analyser for nitrogen oxides (chemiluminescence principle), Horiba APOA 360 analyser for ozone (UV-absorption method) and EMS Andersen Instruments FH62 I-R automatic sampler for particles. SO_2 concentrations were also provided but no interesting results were extracted for this study. Calibration of the equipment was performed by the instruments provider before the experimental campaign, using certified standard gases according to the manufacturer. Additionally, Theodor Friedrichs combined sensors for wind speed and direction as well as for temperature and humidity were used to record meteorological parameters.

Bulk filtration samples were performed on GF 10 fibreglass filters. This fibreglass consists of a selected heavy metal-free basic material. Sampling duration was 24 h with a nominal airflow of 1 m^3/h. Flameless atomic absorption spectroscopy was performed to determine Pb, Cd, Ni while the analysis for Hg and As was based on cold vapour technique and hydride generation, respectively. The detection limits of the methods were—Hg, As and Cd: 0.02 ng/m^3, Pb ∼0.4 ng/m^3 and Ni ∼1.5 ng/m^3.

3. Results and discussion

3.1. Heavy metal concentrations

3.1.1. Variations of Hg, Pb, As, Cd and Ni concentrations in Spata

The daily atmospheric concentrations between 4 June 2003 and 17 June 2003 recorded in Spata are presented in Fig. 2. The highest concentrations were recorded for Ni, with a maximum of 45.1 ng/m^3 and a minimum of 3.49 ng/m^3. As far as Pb is concerned, the concentrations detected during the experimental period were much lower than the limit value of 500 ng/m^3 prescribed by European Council Directive 1999/30/EC (see Fig. 2). Cadmium presented the lowest atmospheric concentrations, reaching average concentration 13 times lower than that of Pb and 30 times lower than that of Ni. Mercury presented similarly low concentrations accordingly. Concerning the wind speed and direction, all four maximum concentrations were detected during days with relatively low wind speeds (3.14–3.73 m/s) blowing from the NE or NNE direction. This is a typical wind pattern in the area since the Evoikos Gulf sea breeze influences

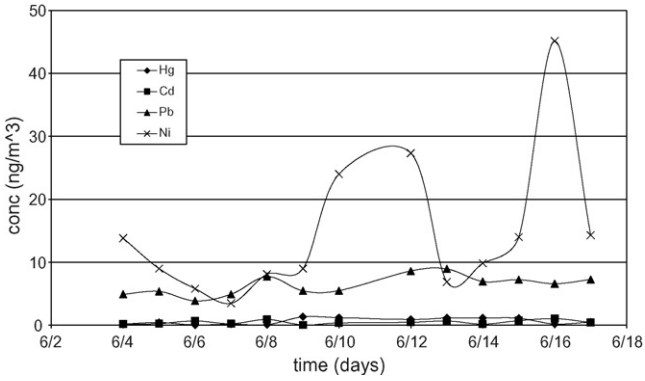

Fig. 2. Heavy metal variations in Spata during summer 2003.

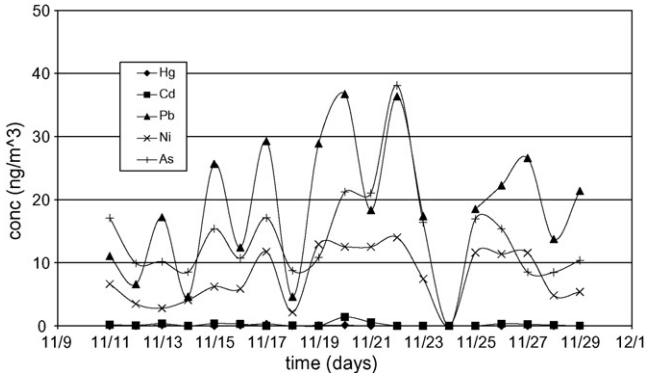

Fig. 3. Heavy metal variations in Spata during winter 2003.

surface flow over the Messogia Plain, when low background flow is prevailing. As a result, pollutants emitted in the NE direction are transported over the measuring region. In this case, the high concentrations can likely be attributed to building construction works taking place in the vicinity of the sampling site during the experimental period.

The daily atmospheric concentrations between 11 November 2003 and 29 November 2003 in Spata are given in Fig. 3. The highest concentrations were recorded for Pb, with maxima much lower than the EU limit value (500 ng/m^3). During this period, Hg presented the lowest atmospheric concentrations, which were 140 times lower than that of Pb and 58 times lower than that of Ni, while Cd presented similar variation. Occasionally, this was the first experimental campaign during which As was detected, implying the predominance of different sources as well as variability in PM transportation during the two periods. Concerning the wind speed and direction, all five maximum concentrations were observed during days with relatively low, W or WNW winds.

In both experimental periods in Spata station, the levels of heavy metal concentrations were not significant with respect to local air quality or public health. Comparing the two periods, these concentrations presented a quite different attitude. Pb definitely increased during the winter period, reaching values three to four times higher than the ones measured during the summer, while a clear increase was also detected for As. On the contrary, Hg, Cd and Ni presented lower concentrations during the winter experimental campaign. Changes in local emissions during the two periods as well as heavy metal transportation appear to be responsible for these differences. In particular, winter period (especially November) in the greater Messogia Plain is characterized with intense grape bushes burning, which seems to be responsible for the increase of Pb and As concentrations, since these heavy metals are strongly related to wood burning [18,21]. Additionally, wind flow during winter is usually characterised by a predominantly NE stable flow, which is responsible for the pollutant dilution in general.

3.1.2. Variations of Hg, Pb, As, Cd and Ni concentrations in Koropi

Fig. 4 summarizes the daily atmospheric concentrations of Hg, Pb, Cd, Ni, which were recorded in Koropi during the sam-

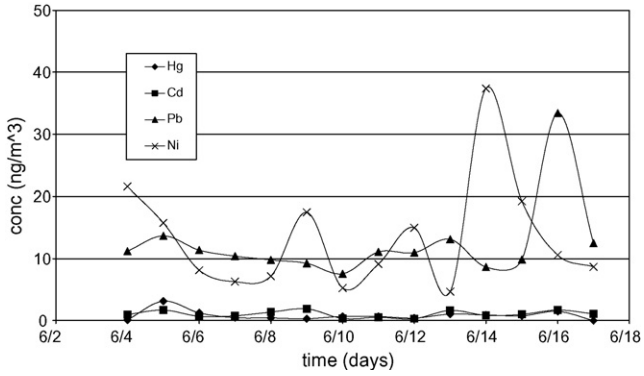

Fig. 4. Heavy metal variations in Koropi during summer 2003.

pling period between 4 July 2003 and 17 June 2003). In this case, the highest concentrations were detected for Ni, while Pb values never exceeded the EU limit value (500 ng/m^3). The mean atmospheric concentrations for the sampling period were 0.89, 1.06, 12.3 and 13.3 ng/m^3 for Hg, Cd, Pb and Ni, respectively. Hg and Cd presented the lowest atmospheric concentrations during this experimental period, with Hg average being 15 times lower than that of Pb and 16 times lower than that of Ni. Regarding the wind pattern, Ni, Hg, Pb and Cd maxima were detected during days with relatively low, NE or ENE winds. Considering the location of the sampling site with respect to the local landscape (flat terrain with no physical obstacles), pollutant transportation might be responsible for these maximum concentrations in Koropi. Once again, the Evoikos Gulf sea breeze played a significant role, since both Attiki Odos (highway with intense vehicular traffic especially during rush hours) and the AIA (permanent source of fuel burning products such as Pb) are located on the NE direction. Additionally, the works taking place along Attiki Odos serving the region, have to be taken under consideration, due to the fact that this highway is closer to the Koropi site (see Fig. 1) and presents high traffic levels during the day.

The daily atmospheric concentrations of Hg, Pb, Cd and Ni, which were recorded in Koropi during the sampling period between 11 November 2003 and 28 November 2003 are presented in Fig. 5. During this period Pb presented the highest values, not exceeding the EU limit. The mean atmospheric concentrations for the sampling period were 0.16, 0.35, 24.7, 7.15 and 4.62 ng/m^3 for Hg, Cd, Pb, Ni and As, respectively. Once again, Hg and Cd reached the lowest atmospheric concentrations with Hg values 176 times lower than that of Pb and 51 times lower than that of Ni. Concerning the wind speed and direction, the maximum concentrations for Ni, Hg, Pb and Cd were detected during days with low WNW winds. On the contrary, minimum concentrations were measured during days with slightly stronger NNE winds (except for Ni which reached its minimum value on the 16th of November, when WNW winds were prevailing). Despite the fact that higher concentrations were observed during days with generally lower winds (as expected), definite conclusions cannot be drawn regarding the correlation between wind speed and heavy metals concentrations. The reason for this is that wind speed presented a weak variation (<1.21 m/s) during the 15 days of the experimental campaign. Thus, the effect of windborne transportation could not be examined with the demonstration of wind velocity.

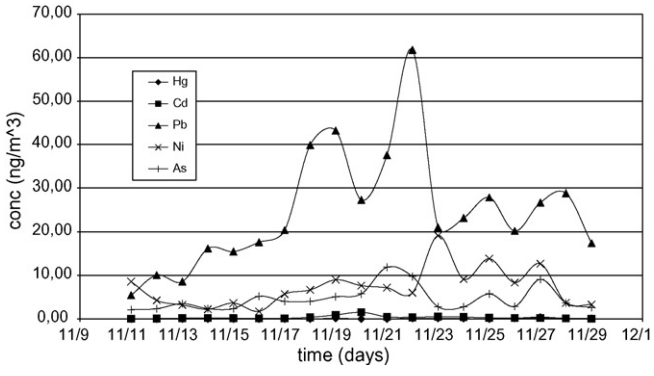

Fig. 5. Heavy metal variations in Koropi during winter 2003.

On the other hand, interesting remarks can be drawn by the examination of wind direction. In particular, the SWTF, located to the WNW of the sampling site in Koropi appears to play an important role in the maximum heavy metal concentrations observed during some of the days with WNW winds, such as the 16th of November. Additionally, the primary road connecting Koropi with other urban areas is located 50 mW of the sampling site and could also be responsible for the detected maxima.

The Hg, Cd and Ni mean values were slightly lower compared to those of the summer campaign, whereas the average Pb concentration was two times higher. In Spata, As concentrations were below detection limits during the summer campaign, but above detection limits during the winter campaign. A possible source of the As in the wintertime could be agricultural burning [15], which is very usual during this period of the year.

3.2. Relationship between heavy metals, meteorological parameters, gaseous pollutants and PM_{10}

Table 2 presents the correlation coefficients between the heavy metal concentrations and meteorological parameters as well as gaseous pollutants, for both sampling sites and periods. The Spearman correlation method has been followed since available raw data referred to a relatively short time period. Marked correlations in Table 2 are significant at p-level <0.05.

As far as the correlation with meteorological parameters and gaseous pollutants is concerned, better correlation was observed during the winter period for both sites. Heavy metal concentration and both meteorological parameters and pollutant concentrations in Koropi, were better correlated during winter than during summer (see Table 2). Heavy metals were definitely not correlated with wind speed (WS) in any case. The only exception was detected in Koropi, where Ni ($r = -0.55$) and Cd ($r = -0.48$) were negatively correlated with WS during the winter period as expected, since increased WS values are usually responsible for the dilution and diffusion of gaseous and particulate pollutants [40,41]. Additionally, Relative Humidity (RH) correlation with Pb ($r = 0.5$), Hg ($r = 0.65$) and As ($r = 0.51$) in Koropi during the winter period was significantly higher than the

Table 1
Average, minimum and maximum heavy metals (Hg, Pb, Cd, Ni) and As concentrations and other pollutants (PM_{10}, NO, NO_2, O_3) in Spata and Koropi for both experimental periods

Site	Hg (ng/m^3)	Cd (ng/m^3)	Pb (ng/m^3)	Ni (ng/m^3)	As (ng/m^3)	PM_{10} (μg/m^3)	NO (μg/m^3)	NO_2 (μg/m^3)	O_3 (μg/m^3)	WS (m/s)	RH (%)	Temperature (°C)
Spata (summer)												
Average	0.66 ± 0.50	0.49 ± 0.31	6.41 ± 1.54	14.7 ± 11.4	nd[a]	19.1 ± 3.3	3.63 ± 1.54	18.2 ± 8.5	140 ± 12	3.30 ± 0.64	34.7 ± 6.5	27.1 ± 1.8
Minimum	0.05	0.05	3.87	3.49	nd	13.3	2.49	11.9	113	1.80	27.5	24.3
Maximum	1.35	1.07	8.95	45.1	nd	24.8	7.83	39.9	156	4.06	50.1	29.4
Spata (winter)												
Average	0.14 ± 0.10	0.34 ± 0.40	19.5 ± 9.8	8.18 ± 4.0	14.7 ± 7.3	56.2 ± 24.7	17.4 ± 12.1	27.8 ± 14.4	41.6 ± 17.3	1.62 ± 0.67	78.3 ± 7.7	14.5 ± 2.3
Minimum	0.09	0.04	4.63	2.17	8.48	16.4	1.28	7.42	6.32	0.76	65.3	9.32
Maximum	0.32	1.40	36.7	14.0	38.1	109	36.6	50.8	68.4	2.78	91.9	17.5
Koropi (summer)												
Average	0.89 ± 0.77	1.06 ± 0.52	12.3 ± 6.3	13.3 ± 8.8	nd	56.9 ± 15.3	1.81 ± 0.34	11.3 ± 2.8	110 ± 11	1.49 ± 0.57	32.9 ± 7.2	27.1 ± 1.8
Minimum	0.11	0.31	7.56	4.67	nd	34.1	1.47	7.92	92.3	0.60	25.6	23.9
Maximum	3.14	1.89	33.4	37.4	nd	87.4	2.58	16.3	125	2.70	50.6	29.6
Koropi (winter)												
Average	0.16 ± 0.10	0.35 ± 0.36	24.7 ± 13.6	7.15 ± 4.42	4.62 ± 2.79	57.6 ± 21.4	9.96 ± 4.85	26.7 ± 8.5	35.1 ± 11.7	0.64 ± 0.25	75 ± 7	14.2 ± 2.1
Minimum	0.09	0.05	5.44	1.72	2.10	21.8	1.73	12.2	17.9	0.28	59.7	9.65
Maximum	0.41	1.53	61.8	19.2	11.9	94.3	15.1	39.0	62.9	1.21	84.3	17.7

Wind speed, wind direction, relative humidity and temperature are also presented.
[a] Not detected.

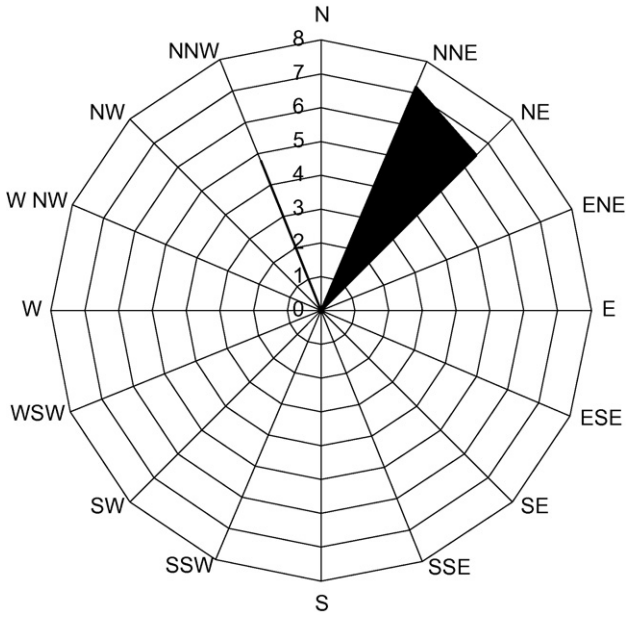

Fig. 6. Pb concentrations in relation with WD in Spata during summer 2003.

one observed in Spata in both winter and summer experimental campaigns (Table 2). This can be attributed to the increased RH levels in a flat, agricultural terrain such as Koropi, especially during winter when RH levels are higher (Table 1). Heavy metals correlations with temperature indicated strong relationship with Pb in Spata during summer period ($r = 0.82$), less so in Koropi during the winter ($r = 0.69$). Finally, wind direction (WD) seemed to influence heavy metal concentrations, since maximum observed values were strongly related to the prevailing winds observed during the experimental period. In particular, summer period was characterized with heavy metal maxima during days with NE or NNE prevailing winds for both sites, strongly influenced by the Evoikos Gulf sea breeze blowing from the NE direction (see Fig. 6 for Pb). Respectively, winter period maxima were recorded during days with W or WNW prevailing winds, which are the predominant winds of this period of the year (see Fig. 7 for Pb). This observation is strongly attributed to the different sources which were prevailing during the two periods, implying an important role for windborne transportation [23].

Concerning the relationship with gaseous pollutants, heavy metals were positively correlated with NO_x in both sites and for both periods, while negative correlation was observed with O_3 as expected, since O_3 is produced directly by photolysis of NO_2 and usually follows an opposite variation [42]. In general, as presented in Table 2, stronger relationship between heavy metals and gaseous pollutants was observer during the winter experimental campaign for both sites.

The percentages of the heavy metal content in PM_{10} total mass for both sites and periods are presented in Table 3. As shown, during the winter experimental campaign, Hg and Cd percentage was an order of magnitude lower than that of the summer campaign, while the corresponding values for Ni followed a similar attitude. On the other hand, Pb percentage presented a significant increase during the winter, following an opposite

Table 2
Correlation coefficient between heavy metals (ng/m^3), meteorological parameters and gaseous pollutants in both sites and for both periods

	PM_{10} (μg/m^3)	NO (μg/m^3)	NO_2 (μg/m^3)	O_3 (μg/m^3)	WS (m/s)	RH (%)	Temperature (°C)
Spata (summer)							
Hg	−0.23	−0.33	−0.36	0.33	−0.07	−0.09	**0.53**
Cd	−0.17	−0.13	−0.30	0.18	0.22	−0.16	0.34
Pb	0.06	**−0.56**	**−0.55**	**0.54**	0.03	−0.09	**0.82**
Ni	−0.08	0.06	−0.33	−0.05	−0.37	0.45	0.22
Spata (winter)							
Hg	0.03	0.23	0.40	−0.16	−0.10	−0.38	0.10
Cd	−0.07	−0.08	−0.07	−0.15	−0.03	−0.07	−0.13
Pb	**0.59**	**0.47**	**0.46**	−0.39	−0.33	0.41	0.28
Ni	**0.62**	**0.64**	**0.54**	**−0.57**	−0.25	0.32	0.20
As	0.33	0.41	0.36	−0.29	−0.07	0.15	−0.01
Koropi (summer)							
Hg	−0.07	−0.25	−0.24	−0.05	−0.12	−0.04	0.09
Cd	−0.17	0.00	0.21	−0.41	−0.21	−0.02	−0.03
Pb	0.35	0.24	0.19	−0.42	−0.33	0.47	−0.21
Ni	0.22	0.11	0.00	−0.13	0.00	−0.04	0.02
Koropi (winter)							
Hg	0.39	0.22	0.08	−0.36	−0.39	**0.65**	0.24
Cd	**0.57**	**0.52**	**0.50**	−0.41	**−0.48**	0.25	0.21
Pb	**0.69**	**0.65**	**0.56**	**−0.50**	−0.24	**0.50**	**0.69**
Ni	**0.64**	**0.53**	**0.47**	**−0.61**	**−0.55**	0.41	0.12
As	**0.73**	**0.79**	**0.70**	**−0.54**	−0.32	**0.51**	**0.50**

Bold figures mean a $p < 0.05$.

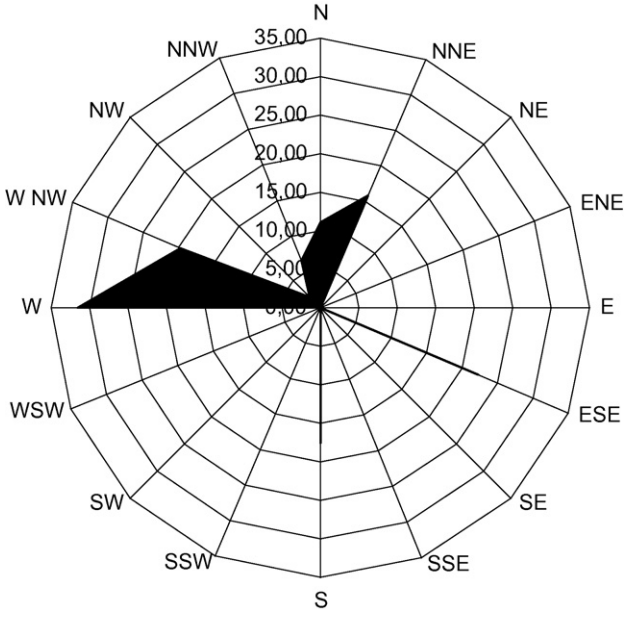

Fig. 7. Pb concentrations in relation with WD in Spata during winter 2003.

Table 3
Comparison of the percentages of the heavy metal content in PM_{10} for both sites and sampling periods

	Hg PM_{10}	Cd PM_{10}	Pb PM_{10}	Ni PM_{10}	As PM_{10}
Spata (summer)	0.0035	0.0025	0.0335	0.0767	
Koropi (summer)	0.0016	0.0019	0.0217	0.0234	
Spata (winter)	0.0003	0.0006	0.0347	0.0145	0.0262
Koropi (winter)	0.0003	0.0006	0.0428	0.0124	0.0080

variation and implying the predominance of different particulate sources during the two seasons. Agricultural and wood burning might be responsible for the increase of Pb concentrations during the winter period [22].

3.3. Comparison of the two sites

3.3.1. Summer period

Data analysis for both sampling sites led to interesting conclusions regarding the comparison of the two locations for the summer period. The Greater Messogia Area was characterized by intense activity related to constructions taking place along Attiki Odos in the NE direction, while the AIA was also located in the same direction. The Evoikos Gulf sea breeze transported air masses from both these permanent sources over the Koropi area. On the other hand, such a mechanism was not working for Spata since both Attiki Odos and the AIA are located in the SW direction.

As a result, the average Pb concentration in Koropi (12.3 ng/m^3) was twice as the corresponding value in Spata (6.41 ng/m^3). In particular, the highest Pb values were recorded in Koropi on the 16th of June, when ENE winds were blowing from the Evoikos Gulf, while the highest value in Spata was recorded on the 13th of June, when the winds were mainly from the N and NE direction. The lowest atmospheric Pb concentrations at Spata and Koropi were recorded on the 6th (NNW) and 10th (ENE) of June, respectively. In general, a higher variability in Pb concentrations was detected in Koropi where Pb values varied between 7.56 and 33.40 ng/m^3, while lower Pb concentration variability was observed in Spata (3.87–8.95 ng/m^3).

As far as Cd is concerned, lower concentrations were measured in Spata, where Cd values exceeded unity only once. In particular, Cd reached its maximum value (1.07 ng/m^3) on the 16th of June, when the Ni maximum concentration was also observed. On the other hand, Cd in Koropi reached its maximum value (1.89 ng/m^3) on the 9th of June, when Ni concentration also reached relatively high levels. Generally, atmospheric concentrations of Cd did not present high variability at either sampling site.

The highest atmospheric Ni concentration was recorded in Spata on the 16th of June when NE winds were prevailing. Fluctuations observed in Ni concentrations were not well correlated with wind direction. In fact, high Ni values were recorded for all northern wind directions, indicating that a variety of local sources contribute to the observed heavy metal concentrations.

3.3.2. Winter period

Average values for all five heavy metals were generally low. Both sites seemed to exhibit similar patterns concerning the fluctuations of the pollutants' values during the experimental period. The average Pb concentration in Koropi (24.7 ng/m^3) was higher than in Spata (19.5 ng/m^3) and this difference in Pb values between the two sites can likely be attributed to local or peripheral sources. A further examination of daily averaged metal values in Koropi shows that maxima were observed during days with WNW winds. The primary road (50 m from the site) as well as the SWTF, both located to the W of the site seemed to be responsible for the maxima detected. Additionally, intense building construction activity was taking place in Spata nearby the sampling site during the experimental campaign and contributed to the observed levels. Taking under consideration that the sampling site is located in the E sector of the town, higher metal concentrations were expected during days with W prevailing winds. This is exactly what was observed during the winter experimental period. Moreover, a primary road 20 m Westerly of the site might also be responsible for the maximum metal concentrations during days with Western winds.

The daily variations of atmospheric concentrations for heavy metals are presented in Figs. 3 and 5. The highest Pb value (61.8 ng/m^3) in Koropi was detected on the 22nd of November when WNW winds were prevailing, while the corresponding value (36.7 ng/m^3) in Spata was recorded on the 20th of November, when the winds were mainly from the WNE direction. Additionally, relatively high atmospheric Pb concentrations were detected in both sites on the same date (November 22nd). In this case, prevailing winds for both sites were blowing from the W sector. Cd reached its maximum value (1.40 ng/m^3) on the 20th of November in Spata, while the maximum Cd concentration in Koropi (1.53 ng/m^3) was observed during the same day. Generally, Cd atmospheric concentrations did not present high variability at either site during the winter period. The highest Ni concentration (19.2 ng/m^3) was recorded in Koropi on the 23rd of November, when WNW winds were prevailing. Fluctuations detected in Ni concentrations were not well correlated with wind direction. However, high Ni values were recorded during days with W or WNW prevailing winds, owing at local sources.

Regarding Hg concentrations, all recorded values remained below the detection limit during most of the experimental days, never exceeding 0.35 ng/m^3. Thus, Hg presented the lowest concentrations of all five metals measured in the campaign. Moreover, both sites presented the same behaviour with maximums detected during days with W prevailing winds. Compared to the summer campaign, Hg concentrations remain at low levels at both sites.

Concerning As concentrations, a maximum value on the order of 38.1 ng/m^3 was recorded in Spata on the 22nd of November, when prevailing winds were blowing from the W sector. Maximum concentrations of Pb and Ni were also observed during the same day. Additionally, the minimum As value (8.48 ng/m^3) was detected on the 28th of November when southern winds were prevailing. On the other hand, lower As concentrations were detected in Koropi. In particular, a maximum of 11.9 ng/m^3 was observed on the 21st of November, when prevailing winds were from the west-northwestern direction. Most of the minimum As concentrations were observed during days with northern prevailing winds.

4. Conclusions

- The highest atmospheric Pb concentrations never exceeded the limit established by the European Union (500 ng/m^3) at either site during either experimental period. In particular, the maximum Pb value in Spata reached 8.95 and 36.7 ng/m^3 for the summer and winter periods, respectively. Additionally, maximum Pb concentrations detected in Koropi were 33.4 ng/m^3 for the summer period and 61.8 ng/m^3 for the winter period.
- Concerning the correlation between heavy metal concentrations and meteorological parameters, better correlation was observed during the winter period for both sites. Heavy metal concentrations in Koropi, presented higher correlation with meteorological parameters during the winter experimental campaign, compared to the correlation estimated during the summer period (Table 2). Heavy metals were not well correlated with WS. On the other hand, RH presented a higher correlation with Pb ($r = 0.5$), Hg ($r = 0.65$) and As ($r = 0.51$) in Koropi during the winter period than the corresponding correlation detected in Spata during both sampling periods (Table 2). Heavy metal correlations with temperature indicated a strong relationship with Pb in Spata during the summer period ($r = 0.82$), while correlation with Pb was also observed in Koropi during the winter ($r = 0.69$). WD seemed to influence heavy metal concentrations since maximum observed values were strongly related to the prevailing wind direction observed during each experimental period. In particular, during the summer period, maximum concentrations for all heavy metals were observed during days with NE or NNE prevailing winds for both sites. Respectively, the winter period maximums were recorded during days with W or WNW prevailing winds.
- NO presented a strong correlation with heavy metals (apart from Hg) for both sites during winter period. Similar attitude was followed by NO_2 but to a lesser extend. Finally, O_3 was

negatively correlated with heavy metal values as with other gaseous pollutants.

- The total percentage of PM_{10} Hg, Cd and Ni contained in PM_{10} total mass, presented a strong variation for both sites and experimental periods. In particular, during the winter experimental campaign the PM_{10} Hg percentage was an order of magnitude lower compared to that estimated during the summer period, with Cd and Ni presenting a similar picture. This indicated that PM_{10} sources were different during summer and winter. On the other hand, the Pb percentage was increased during the winter campaign. This also fortifies the hypothesis that different heavy metal sources were prevailing during the two seasons.

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