

CONCENTRATION MEASUREMENTS AND CHEMICAL CHARACTERIZATION OF PM_{2.5} AT AN INDUSTRIAL COASTAL SITE IN SARONIC GULF, GREECE

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ABSTRACT

Aerosols samples of PM_{2.5} were collected during October 2004 in the industrial zone of the greater Athens area, located in the coastal region of Saronic Gulf, westerly of the city. In particular, two different sites were selected, in order to obtain experimental data from: a) the shoreline, where industrial activity and vehicular traffic were intense, and b) the mainland, where residential activity and low vehicular traffic were prevailing.

Two low volume (2.3 m³ hr⁻¹) Derenda particulate samplers were used in 24-hour basis as well as Tissue Quartz 0,47mm filters for the sample collection. After the collection, filters were stored in a conditioning room (T=20°C and RH=50%) for 24 hours and weighted with the use of MX-5 Mettler Toledo Microbalance (10⁻⁶ gr sensitivity), in order to estimate the daily PM_{2.5} concentrations. SO₄²⁻, NO₃⁻ and Cl⁻ anions and Na⁺, K⁺, NH₄⁺, Mg²⁺ and Ca²⁺ cations concentrations were estimated, following the Ionic chromatography method.

According to the results, PM_{2.5} mean concentration in the shoreline reached 46.5 µg m⁻³, while the corresponding value for the mainland was 39.0 µg m⁻³. Na⁺ cations and SO₄²⁻ anions presented greater concentrations than all the others cations and anions in both areas. In particular, Na⁺ cations concentrations in the shoreline varied between 13.2 and 5.72 µg m⁻³, while SO₄²⁻ anions between 29.5 and 16.6 µg m⁻³. The respective values in the mainland varied between 11.8 and 8.32 µg m⁻³ for Na⁺ cations and between 28.0 and 4.46 µg m⁻³ for SO₄²⁻ anions. All the other ions concentrations varied in levels 2 – 3 classes of magnitude lower than the ones observed for Na⁺ and SO₄²⁻. As far as the percentage of ions in the total PM_{2.5} average concentration in the shoreline is concerned, Na⁺ cations consisted the 22% of the total concentration, while SO₄²⁻ anions consisted the 55%. The corresponding values for the mainland were 24% and 37%.

It is the purpose of this work to demonstrate the concentration levels as well as the chemical composition of PM_{2.5} measured in areas where intense emission rates are observed. Additionally, the transportation of these pollutants is going to be examined, in order to evaluate the influence in residential regions nearby the industrial areas, taking under consideration the meteorological parameters and the atmospheric circulation conditions, such as sea breezes, which prevail in coastal areas.

KEYWORDS: PM_{2.5}, anions, cations, meteorology, industrial, coastal and residential areas

1. INTRODUCTION

PM_{2.5} particles arise in the air either as direct emission from natural and anthropogenic sources, or as a result of interactions of pollutants in the atmosphere. In particular, under real world conditions vehicular particle emissions are the result of different processes, e.g. combustion products from fuel and oil, wear products from brake linings, tyres, bearings, coach and road construction material and the re-suspension of road and soil dust. Furthermore, ageing effects like adsorption and photochemical reactions after the emission influences particulate matter may occur (Weingartner *et al.*, 1997). They are known to have numerous negative health effects such as bronchitis and asthma (Finlayson-Pitts and Pitts, 1999) since they are small enough to penetrate into the lungs. As a result the investigation of the chemical composition of PM_{2.5} has recently become very significant.

Very little is known about emission and aerosol composition over the Eastern Mediterranean since only a small number of studies on PM were conducted in the region. Particularly in Greece the chemical composition study of aerosols showed that oxalate and ammonium sulfate constituted the main organic and inorganic ionic species respectively, with the latter accounting for 90% of the total ionic mass in fine fraction (Bardouki *et al.*, 2003).

Additionally, the composition of individual marine aerosols in Israel was studied using scanning electron microscopy, ion chromatography and transmission electron microscopy techniques (Ganor *et al.*, 1998). Results showed that calcium sulfate, sodium sulfate and sulfuric acid were the main constituents of aerosols during the sea breeze. However, during the land breeze, particles such as sulfates, nitrates, phosphates and trace elements, stemming from industries, increased in concentrations.

2. MATERIALS AND METHODS

2.1 Site Description

Eleusina is a small town of 15000 inhabitants, lying in the outskirts of Athens approximately 20Km westerly – northwesterly of the city centre. As shown in figure 1, the town is located in the greater Attica basin surrounded by high mountains from the three sides (Eastern, Northern and Western section), while the fourth side is open to the sea (Southern section). The climate of the area is typically Mediterranean with hot, dry summers and wet, mild winters (Katsoulis, 1988). The mean daily summer temperature is 25.8° C, while the mean annual precipitation is about 400mm and occurs during the fall and winter months. The mean wind pattern in the atmospheric boundary layer in the vicinity of the Eleusina region can be characterised by a predominantly north-eastern flow. The area is exposed to the summer monsoon circulation driven by the Arabian heat low. The resulting northern winds in the Aegean, called the Etesians, are occasionally interrupted by the passage of weak pressure troughs (Reparis *et al.*, 1997; Katsoulis, 1988). In this case, a southern sea-breeze circulation is developed in Eleusina coming from the Saronic Gulf, a situation associated with photochemical pollution episodes.

Concerning the town itself, it is separated in two parts considering the land use and the local characteristics: a) the industrial section (site A), which is located across the shoreline and is the main source of pollutants in the area in a 24-hour basis and b) the residential section (site B), which is lying over the mainland in the northern part of the region, with two or three floor, detached residencies. The two sections are separated by the National Highway, a two ways, high velocity, busy road, which connects Athens with the western provinces of the country.

2.2 Instrumentation and Methodology

Two low volume (2,3 m³ hr⁻¹) Derenda particulate samplers operated in 24-hour basis using Tissue Quartz 0,47mm filters for the PM_{2.5} collection. Sampling in A was carried out at the top of a small ISOBOX container sited approximately 50 meters away from the National Highway to the northern direction.

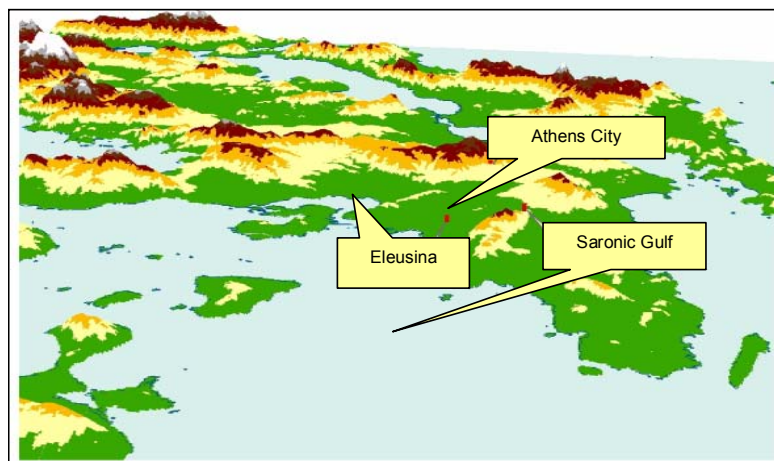


Figure 1. Map of Eleusina site in the Attica Basin

Large industries operating in 24 - hour basis were located on the opposite side of the highway 90 meters away from the container to the southern direction. Respectively, measurements in B were conducted on a flat area close to municipality of Eleusina, about 1200 m from A to the northern direction. The area was surrounded by two or three floor, detached residencies, while the low vehicular traffic and the absence of high volume emitting sources, such as industries were the main characteristics of the site. After the collection, filters were stored in a conditioning room ($T=20^{\circ}\text{C}$ and $\text{RH}=50\%$) for 24 hours and weighted with the use of MX-5 Mettler Toledo Microbalance (10^{-6} gr sensitivity), in order to estimate the daily $\text{PM}_{2.5}$ concentrations. SO_4^{2-} , NO_3^- and Cl^- anions and Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+} cations concentrations were estimated, following the ionic chromatography method. In particular, for the cations analysis a Waters system for ionic chromatography was used, while for the corresponding anions the system was a 761 Compact IC of Metrohm.

Finally, meteorological parameters were continuously recorded by instrumentation provided by the Hellenic National Meteorological Service, operating in close proximity with A and B sites. In particular, wind speed and direction were measured with the use of a cup and a vane anemometer respectively, while temperature and relative humidity were observed with specialized sensors.

3. RESULTS AND DISCUSSION

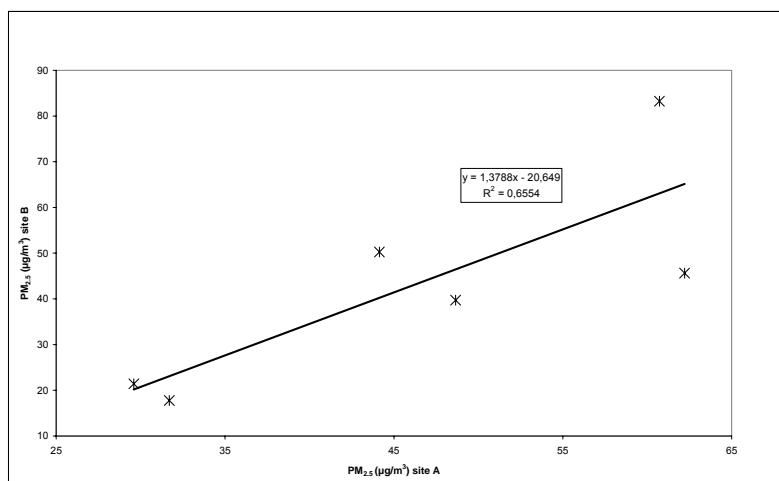
3.1 $\text{PM}_{2.5}$ Variations

Table 1 summarizes the average $\text{PM}_{2.5}$ concentrations for the two sites and for the whole experimental period. The average $\text{PM}_{2.5}$ concentration during the sampling period was $43.81 \mu\text{g m}^{-3}$ for site A and $43,01 \mu\text{g m}^{-3}$ for site B. Until now the European Union has not established an ambient air quality standard for $\text{PM}_{2.5}$. However, the United States EPA daily $\text{PM}_{2.5}$ standard is $65 \mu\text{g m}^{-3}$. $\text{PM}_{2.5}$ average concentrations in both sites did not exceed this value. Therefore, only in one case (Saturday 9th of October) in site B, $\text{PM}_{2.5}$ concentration reached $83.26 \mu\text{g m}^{-3}$, which is probably due to a local source existing only for this day. Finally, $\text{PM}_{2.5}$ average concentrations during weekdays did not present any differences with the corresponding concentrations observed during weekends. This can be attributed to the fact that both industries and the national highway, which are the main $\text{PM}_{2.5}$ sources in the greater Eleusina area, present continuous activity in twenty four hour basis. Nevertheless, the national highway presents more intense vehicular traffic during the weekends, since a large part of Athens residents usually abandon the capital city for the province.

Figure 2 presents the correlation pattern between $\text{PM}_{2.5}$ concentrations in sites A and B. As it is shown, the recorded values were not very well correlated ($r^2 = 0.66$), despite the fact that the average concentrations presented similar variations and almost the same average value for the whole experimental campaign. This shows that the impact of the neighboring sources and local activity on sites A and B is quite different, mainly depending on local circulation.

Table 1. PM_{2.5} concentrations for the whole experimental campaign and for both sites

Date	Day	PM _{2.5} site A ($\mu\text{g m}^{-3}$)	PM _{2.5} site B ($\mu\text{g m}^{-3}$)
8/10	Friday	48,65	39,73
9/10	Saturday	60,72	83,26
10/10	Sunday	44,14	50,26
11/10	Monday	62,21	45,64
12/10	Thursday	29,66	
13/10	Wednesday	29,6	21,42
14/10	Thursday	31,7	17,76
	min	29,60	17,76
	max	62,21	83,26
	ave	43,81	43,01

Figure 2. Correlation between PM_{2.5} concentrations in sites A and B

3.2 Daily Ionic Variations

Tables 2 and 3 present all the ionic species daily concentrations detected in the two sites of the whole experimental campaign. Additionally, minimum, maximum and average values have also been estimated. According to the results, SO_4^{2-} anions presented the greater daily variations than all the other cations and anions in both areas, varying between 29.5 and 16.6 $\mu\text{g m}^{-3}$ in A and between 28.0 and 4.46 $\mu\text{g m}^{-3}$ in B. The average SO_4^{2-} percentage in the total ionic mass was 60% for A and 48% for B. The difference in the two percentages was due to the location of the two sites, since A was located closer to the industrial zone, which was considered as the main source of SO_4^{2-} . Furthermore, Na^+ cations presented high concentrations in both sites, varying between 13.2 and 5.72 $\mu\text{g m}^{-3}$ in A and between 11.8 and 8.32 $\mu\text{g m}^{-3}$ in B. In this case, the corresponding Na^+ mass accounted for up to 24% of total ionic mass in A and 32% in B. The lower percentage recorded in A, in this case, is a clear indication about the different sources, which are responsible for the ionic emissions. All the other ions concentrations varied in levels 2 – 3 classes of magnitude lower than the ones observed for Na^+ and SO_4^{2-} . In particular, as far as the percentage of ions in the total PM average concentration in the shoreline is concerned, Na^+ cations consisted the 22% of the total concentration, while SO_4^{2-} anions consisted the 55%. The corresponding values for the mainland were 24% and 37%.

Table 2. Ionic concentrations for the whole experimental campaign and for site

Date	Na ⁺ ($\mu\text{g m}^{-3}$)	NH ₄ ⁺ ($\mu\text{g m}^{-3}$)	K ⁺ ($\mu\text{g m}^{-3}$)	Mg ²⁺ ($\mu\text{g m}^{-3}$)	Ca ²⁺ ($\mu\text{g m}^{-3}$)	Cl ⁻ ($\mu\text{g m}^{-3}$)	NO ₃ ⁻ ($\mu\text{g m}^{-3}$)	SO ₄ ²⁻ ($\mu\text{g m}^{-3}$)
10/8	6.41	0.3	0.23	0.47	0.67	0.92	4.63	27
10/9	5.72	0.72	0.27	0.49	0.71	1.53	5.84	28.8
10/10	11.1	0.43	0.27	0.97	1.08	1.42	5.86	27.1
10/11	13.2	0.07	0.29	0.7	0.77	2.3	3.29	29.5
10/12	8.19	0.06	0.17	0.47	0.5	1.16	0.76	18.9
10/13	11.5	0.24	0.23	0.58	1.38	0.96	1.14	20.6
10/14	10.1	0.06	0.22	0.75	0.67	0.64	1.29	16.6
min	5.72	0.06	0.17	0.47	0.5	0.64	0.76	16.6
max	13.2	0.72	0.29	0.97	1.38	2.3	5.86	29.5
ave	9.46	0.27	0.24	0.63	0.83	1.27	3.26	24.1

Table 3. Ionic concentrations for the whole experimental campaign and for site B

Date	Na ⁺ ($\mu\text{g m}^{-3}$)	NH ₄ ⁺ ($\mu\text{g m}^{-3}$)	K ⁺ ($\mu\text{g m}^{-3}$)	Mg ²⁺ ($\mu\text{g m}^{-3}$)	Ca ²⁺ ($\mu\text{g m}^{-3}$)	Cl ⁻ ($\mu\text{g m}^{-3}$)	NO ₃ ⁻ ($\mu\text{g m}^{-3}$)	SO ₄ ²⁻ ($\mu\text{g m}^{-3}$)
10/8	10.3	0.33	0.38	1.2	1.23	0.83	2.53	16.6
10/9	8.72	0.9	0.31	0.83	0.82	0.63	4.65	20.6
10/10	11.4	0.47	0.26	1.19	1.27	1.44	6.04	28
10/11	11.8	0.12	0.23	1.35	1.47	0.68	0.34	21
10/12	10.9	0.14	0.24	1.34	1.25	0.38	0.79	4.46
10/13	11.5	0.08	0.27	1.57	1.46	0.81	4.49	9.18
10/14	8.32	0.06	0.23	1.22	1.19	0.43	1.3	10.5
min	8.32	0.06	0.23	0.84	0.82	0.38	0.34	4.46
max	11.8	0.9	0.38	1.57	1.47	1.44	6.04	28
ave	10.4	0.3	0.27	1.24	1.24	0.74	2.88	15.8

3.3 Factors influencing the variation of main ionic species

Based on the data analysis in relation to the meteorological parameters, it was found that during the experimental campaign three different categories of weather conditions were prevailing: a) the first category consisted of the first three experimental days (8th, 9th and 10th October) and was characterized by weak winds blowing from the southern sector, clearly associated with the development of sea breeze from the Saronic Gulf. In this case, high NH₄⁺ and SO₄²⁻ concentrations were observed in both sites (see figures 3a and 3b). Sea breeze was clearly related to these high concentrations, since it was responsible for the transportation of sea-born air over the industrial zone and then over the two experimental sites. b) The second category consisted of the 11th and 12th October and was characterized by continuous rainfall. As expected, NH₄⁺ and SO₄²⁻ values were quite low, due to the PM absorption by the rain. c) Finally, the third category included the 13th and 14th October, during which strong, northern winds were prevailing. As a result, clean air masses coming from the mainland (mountain with no anthropogenic sources), influenced the experimental sites, giving remarkably low NH₄⁺ and SO₄²⁻ concentrations.

The impact of sea breeze is also proved in figures 4a and 4b, in which NH₄⁺ has been selected as an example in order to present the average concentrations in relation with wind direction. As it is shown, NH₄⁺ concentrations in both sites were significantly raised during days with southwestern prevailing winds, compared to the ones observed during days with winds from the northern sector. Days with rain were subtracted from these figures.

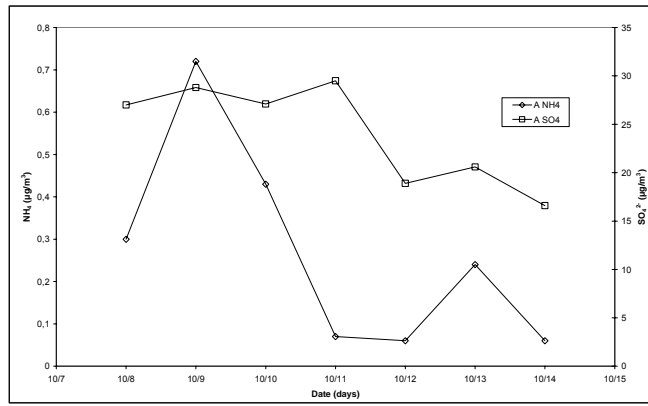


Figure 3a. Daily variations of NH₄⁺ and SO₄²⁻ concentrations in A site

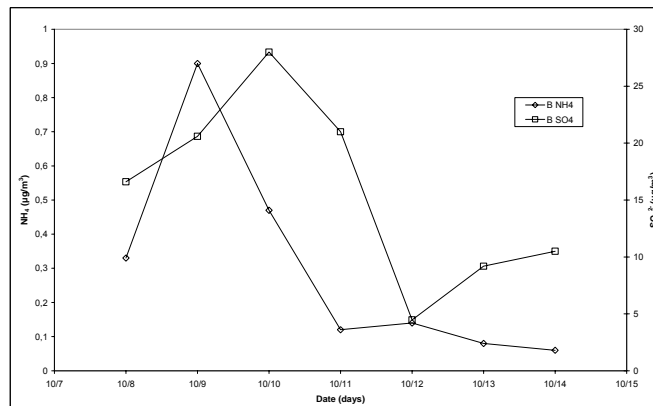


Figure 3b. Daily variations of NH₄⁺ and SO₄²⁻ concentrations in B site.

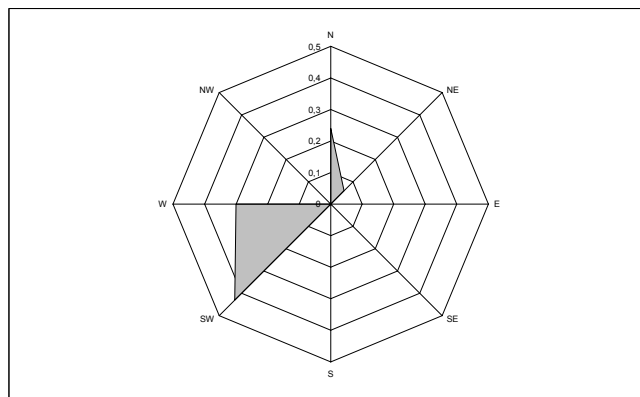


Figure 4a. Average NH₄⁺ concentrations in relation to wind direction for site A

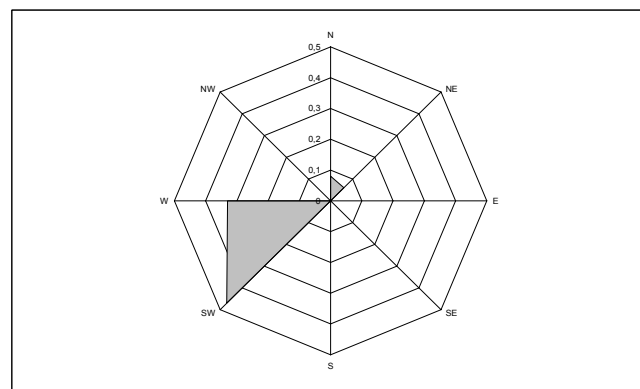


Figure 4b. Average NH₄⁺ concentrations in relation to wind direction for site B

3.4 Interspecies correlation

Several statistically significant ($P < 0.05$, where P is the level of significance at $\alpha = 0.05$) interspecies correlations were observed during the first category of the experimental campaign, during which sea breeze was prevailing. As shown in figures 5a and 5b the relation between Mg^{2+} and Na^+ indicates that both compounds mainly originated from seawater (Bardouki *et al.*, 2003), since the slope of their regression ($Mg^{2+}/Na^+ = 0.10$ for A and $Mg^{2+}/Na^+ = 0.14$ for B) is close to that reported for seawater (mass ratio of 0.12). Corresponding relationship was not observed for Cl^- and Na^+ either in A or in B (figures 6a and 6b). In particular, correlation coefficient for A reached 0.05 while the corresponding Cl^-/Na^+ ratio was 0.03. When compared to the seawater Cl^-/Na^+ (1.8), the above slope indicated no common origin for the two compounds. Despite the fact that the two ion species were very well correlated in B ($r^2 = 0.86$), the same conclusion could be drawn concerning their origin, since the estimated ratio Cl^-/Na^+ was 0.29.

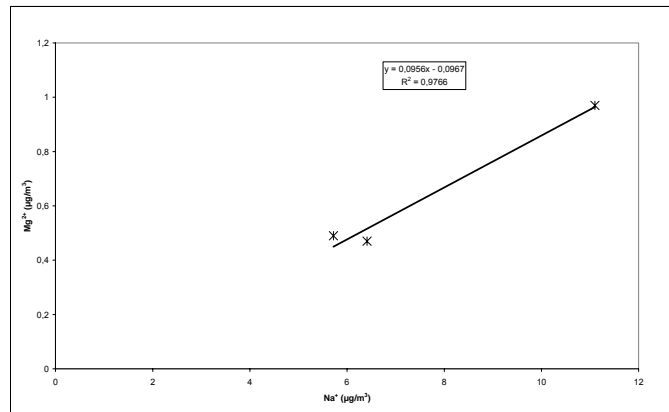


Figure 5a. Correlation between Mg^{2+} and Na^+ for the first category (sea breeze) in site A

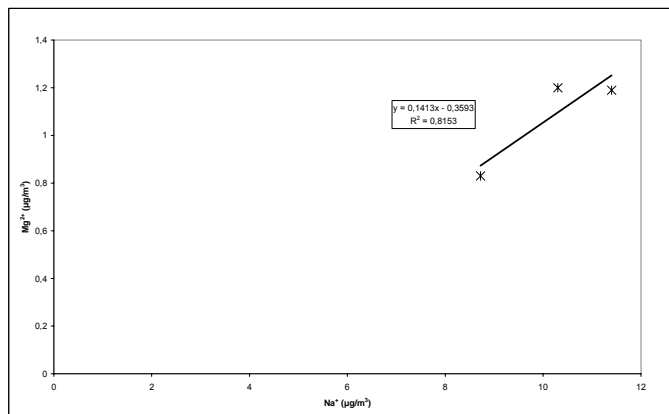


Figure 5b. Correlation between Mg^{2+} and Na^+ for the first category (sea breeze) in site B

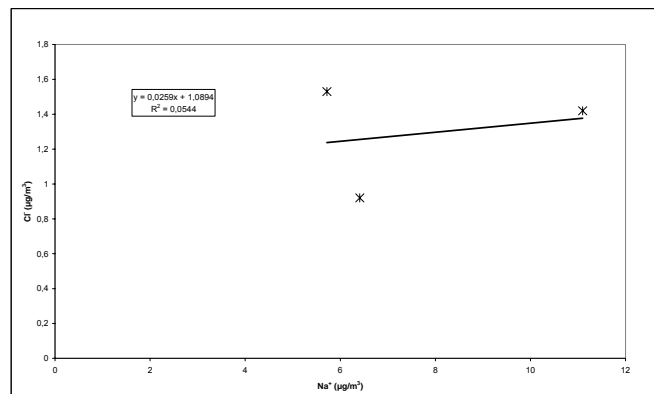


Figure 6a. Correlation between Cl^- and Na^+ for the first weather category (sea breeze) and for A site.

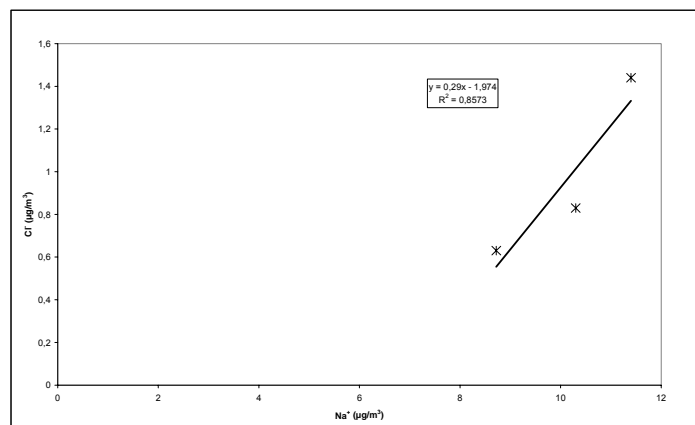


Figure 6b. Correlation between Cl⁻ and Na⁺ for the first weather category (sea breeze) and for B site

4. CONCLUSIONS

Determination of the chemical composition of PM_{2.5} was performed, following the Ionic chromatography method, applied on Tissue Quartz 0,47 mm filters, which were used in two low volume (2,3 l hr⁻¹) Derenda particulate samplers. The sampling was conducted during the period between the 8th and 14th October 2004.

- Na⁺ and SO₄²⁻ compounds accounted for 12 – 32% and 48 - 60% of the total ionic mass respectively, indicating a strong contribution of the industrial zone in the local pollution levels.
- No correlation was observed between all ionic species and atmospheric temperature, relative humidity and wind speed. On the other hand, strong relationship was detected between NH₄⁺ and SO₄²⁻ and wind direction, due to the different characteristics of the air masses, which were coming from the sea (southern sea breeze passing over the industrial area) and from the mainland (strong northern winds).
- Ionic species origin was of great concern during the experimental campaign. According to the results strong correlation was estimated between Mg²⁺ and Na⁺ in both sites, indicating common sources. However, Cl⁻ and Na⁺ presented a satisfactory relation in the shoreline site, but no correlation at all in the mainland site. This observation clearly indicated the existence of different emitting sources close to the two experimental locations.

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