# Chemical composition of wet deposition in a Mediterranean site Athens, Greece related to the origin of air masses

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Abstract The goal of this study is to determine the chemical composition of rain, in the wider region of Athens, Greece for the time period 1st September 2001 to 31st August 2002. Two model automatic rain samplers were installed in the Meteorological Station of Laboratory of Climatology (latitude: 37° 58' N, longitude: 23° 47' E) inside the Athens University Campus and in a site at Heraklio Attica, a northern suburb of Athens (latitude: 38° 03' N, longitude: 23° 45' E). The concentrations ( $\mu$ eq l<sup>-1</sup>) of the major cations (H<sup>+</sup>,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) and anions (Cl<sup>-</sup>,  $NO_3^-$ ,  $HCO_3^ \kappa \alpha \iota$   $SO_4^{2-}$ ), as well as pH and conductivity of rain in 39 total samples were determined. The figures of pH range from 6.4 to 8.4 and conductivity from 8 to 207  $\mu$ S cm<sup>-1</sup>. The analysis showed that Ca<sup>2+</sup> ions are abundant within all examined samples, while  $HCO_3^-$  and  $SO_4^{2-}$  present the highest concentrations from the anions. In order to find out the origin of the air masses, the air mass back trajectories were calculated. Five sectors of the origin of air masses were revealed: the North, the South, the Local, the West and the East sector. Multivariate methods included Factor Analysis and Discriminant Analysis were applied to the examined ion concentrations and three main factors were extracted, which discriminated the ions according to their origin. The first group of ions is interpreted as the result of the anthropogenic activity, the second group represents the acidity-alkalinity independently of their source and the third one the marine influence.

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## **1** Introduction

The phenomenon of acid rain presents great scientific interest, and is well known that it is one of the important environmental problems and for this reason a lot of studies and analyses have been carried out concerning the emissions, the way of transport, transformation and deposition of air pollutants which causes acid rain (Beilke 1983; CEC 1985; Pierson and Chang 1986). Particularly in the central-eastern Mediterranean, acid episodes ( $\sim 25\%$ , pH< 5), and a great percentage (> 40%) of episodes with pH> 6 appeared (Glavas 1988; Dikaiakos et al. 1990; Samara et al. 1992; LeBolloch and Guerzoni 1995; Tuncel and Ungoer 1996; Guelsoy et al. 1999). Also acid and alkaline rains have been reported in Israel (Mamane and Gottlieb 1995), in Spain (Camarero and Catalan 1993; Avila and Alarcon 1999; Hontoria et al. 2003) and in southern France (Loye-Pilo and Morelli 1988). In Greece, the study of the phenomenon of acid rain began 25 years ago, approximately, when some researchers showed scientific interest for the reasons responsible for the observed deterioration of the marbles of Parthenon (Vocom 1979; Skoulikidis 1983; Cheng et al. 1987). Then, a lot of researchers studied systematically the phenomenon of acid rain in Athens (Dikaiakos and Nastos 1987; Dikaiakos et al. 1990; Smirnioudi and Siskos 1992; Kelepertsis et al. 2002; Kita et al. 2004; Nastos et al. 2004), in Thessalonica (Samara et al. 1992), in Patras (Glavas 1988; Glavas and Moschonas 2002), in Crete (Mihalopoulos et al. 1997) and in central Greece (Tsikritsis 2006).

This work presents the results of the chemical composition of the wet deposition, with respect to the concentrations of major anions and cations, in two locations in the wider region of Athens, for the period September 2001–August 2002 and aims in finding out the sources of the ions using multivariate statistical methods and air mass back trajectories.

### 2 Data and analysis

The collection of the rain samples was achieved using prototype automatic samplers, the specifications of which have been reported in previous studies, (Dikaiakos and Nastos 1987; Dikaiakos et al. 1990). The automatic samplers had been installed in the Meteorological Station of Laboratory of Climatology inside the Athens University Campus (latitude: 37° 58' N, longitude: 23° 47' E) and in a site at Heraklio, Attica (latitude: 38° 03' N, longitude: 23° 45' E). Figure 1 depicts the locations of the two rain samplers. The collection of 39 rain samples occurred on 24 hours basis (end of procedure at 08:00 am, local time) during the period from September 2001 to August 2002 and concerns 17 common in both stations and 5 isolated in the one station, precipitation events (Table 2).

The samples of rain were kept in polyethylene bottles (Moody and Lindstrom, 1977) and forwarded in the Laboratory for the chemical analyses. The preparation of samples and the chemical analyses, took place in the Laboratory of Geochemistry of the University of Athens.

The measurements of pH (pH meter Hanna HI 8424) and conductivity (Hanna HI 9033 multi-range conductivity meter) were done at once after the sample collection at 8 o' clock in the morning. The pH meter was calibrated in the range 4–7 before every use. In the process, every rain sample was kept in the refrigerator (4°C) for the chemical analyses forward.

The rainwater samples were vacuum filtered through 0.45  $\mu$ m pore size membrane filters. A part of each sample was vacuum filtered with the same membrane filters and acidified to a final concentration of about 1% nitric acid. In the process, every rainwater sample was kept in the refrigerator (4°C) for the chemical analyses forward. Sulphate, nitrate and chloride were measured photometrically using a Hach DR/2000 apparatus. Bicarbonate was measured using a Hach alkalinity titrator. Calcium and magnesium were measured using an Atomic Absorption Spectrophotometer Perkin Elmer 1100B while sodium and potassium were measured using a flame photometer Jenway PFP7.

The analyses applied to the data under consideration were the Factor Analysis (FA), the Discriminant Analysis (DA) and the back trajectories analysis which are briefly discussed below:

The main applications of FA are to reduce the number of variables and to detect structure in the relationships between variables, that is to classify variables. Therefore FA is applied as a data reduction or structure detection method. Therefore each of the p initial variables  $X_1, X_2, ..., X_p$  can be expressed as a linear function of m (m<p) uncorrelated factors:  $X_i$ =  $a_{i1}F_1 + a_{i2}F_2 + ... + a_{im}F_m$  (i=1,..., p) where  $F_1, F_2, ..., F_m$  are the factors and  $a_{i1}, a_{i2}, ..., a_{im}$  are the factor loadings which express the correlation between the factors and the initial variables. The values of each factor are called factor scores and they are presented in standardized form, having zero mean and unit variance (Jolliffe 1986; Manly 1986). The number m of the retained factors has to be decided, by using various rules (eigenvalue  $\geq 1$ ,



Fig. 1 Locations of the automated rainwater samplers

		Mean	Std. Dev.	Minimum	Maximum
University Campus	pН	7.4	0.4	6.4	8.4
Heraklio, Attica	-	7.4	0.5	6.5	8.1
University Campus	Conductivity( $\mu$ S cm <sup>-1</sup> )	63.4	42.0	10.0	137.0
Heraklio, Attica		88.4	60.4	8.0	207.0

Table 1 Statistical figures for pH and conductivity

scree plot) and considering the physical interpretation of the results (Bartzokas and Metaxas 1993). Another important point of the analysis is the rotation of the axes, which maximizes some factor loadings and minimizes some others and in that way a better separation among the initial variables is succeeded. Varimax rotation is generally accepted as the most accurate orthogonal rotation, which maximizes the sum of the variances of the square factor loadings, keeping the factors uncorrelated (Richman 1986).

Discriminant analysis is useful for situations where the subject of research is to build a predictive model of group membership based on observed characteristics of each case. The procedure generates a discriminant function (or, for more than two groups, a set of discriminant functions) based on linear combinations of the predictor variables that provide the best discrimination between the groups. The functions are generated from a sample of



Fig. 2 Histograms of pH and conductivity for the two sampling sites

function of pH for all rainwater

Fig. 3 Conductivity as a

samples



cases for which group membership is known; the functions can then be applied to new cases with measurements for the predictor variables but unknown group membership.

The application of multivariate analyses was performed by using SPSS for Windows, version 11. All the multivariate methods were applied to the  $\log_{10}$  converted data (Glavas and Moschonas 2002).

First and foremost, using Factor Analysis, three main factors with eigenvalues >1 were evaluated. In the process, the application of Discriminant Analysis to the factor scores extracted by the Factor Analysis resulted in the best discrimination of the main factors between the sectors, which were defined by the analysis of air mass back trajectories. For the calculation of the back trajectories analysis the HYSPLIT 4 model of Air Resources Laboratory of NOAA (Draxler and Hess 1997, 1998) is used for two different levels: 1500 and 3000 m (a.m.s.l.).

## **3 Results and discussion**

Table 1 presents the statistical characteristics of pH and conductivity, for both locations. The pH figures are found in agreement with the respective findings of others researchers (Glavas 1988; Samara et al. 1992; Dikaiakos et al. 1990; Smirnioudi and Siskos 1992; Kelepertsis et al. 2002; Kita et al. 2004).

It is well known that a water solution containing 325 ppm CO<sub>2</sub>, which is approximately the concentration of CO<sub>2</sub> in the atmosphere, presents a typical pH value of approximately 5.6. Rainfall pH figures smaller than the threshold of 5.6 are associated with the effect of natural (such as volcanic emissions) or anthropogenic (such as central heating, transportation and industry emissions) source of pollution. With respect to the examined period (1/9/2001–31/8/2002), episodes of acid rain (pH<5.6) were not recorded in both the two sites of observation. The frequency distribution of pH (Fig. 2) shows that the class 7.5– 8.0 is the prevailing one (39% for University Campus and 38% for Heraklio), meaning a shift to alkalinity compared to the respective frequency distribution for the previous studied period (1/9/2000–31/8/2001), where the class 7.0–7.5 was the predominant regarding 40 rain samples (Kelepertsis et al. 2002). With respect to conductivity histograms (Fig. 2), we observe that the class 0–50  $\mu$ S cm<sup>-1</sup>, dominates (50% for University Campus and 38% for the Heraklio).

Month	11/01	12/01	01/02	02/02	03/02	04/02	05/02	07/ 02	08/ 02	Annual
Number of rainwater samples	12	10	2	2	5	4	2	1	1	39
Rainfall (mm) at the University Campus	154.0	85.4	9.6	7.2	58.8	26.8	35.0	32.0	0.8	409.6
рН	$7.3 {\pm} 0.5$	$7.2 \pm 0.2$	$7.4 \pm 0.3$	$8.0{\pm}0.1$	$7.7 {\pm} 0.6$	$7.7 {\pm} 0.1$	$7.8{\pm}0.4$	7.4	6.5	7.4±0.5
[H <sup>+</sup> ] <sub>Total</sub>	$0.6 {\pm} 0.5$	$0.6 {\pm} 0.4$	$0.7 {\pm} 0.2$	$0.8{\pm}0.0$	$0.6 {\pm} 0.2$	$0.3{\pm}0.5$	$0.5{\pm}0.1$	0.6	0.2	$0.6 \pm 0.4$
Conductivity	$60.8\pm$	$51.9\pm$	$70.0\pm$	$179.0\pm$	$97.8\pm$	$69.5\pm$	$152.5\pm$	136.0	43.0	$76.9\pm$
	48.4	32.0	41.0	17.0	62.4	46.7	31.8			53.5
$[SO_4^{2-}]$	$117.4\pm$	$175.0\pm$	$302.1\pm$	$854.2\pm$	$133.3\pm$	$281.2\pm$	$781.2\pm$	479.2	187.5	$246.7 \pm$
	158.5	180.1	250.4	206.2	95.0	270.8	132.6			265.1
$[NO_3^-]$	$28.3\pm$	$36.1\pm$	$46.1\pm$	$106.8 \pm$	$61.3\pm$	$49.0 \pm$	$244.8 \pm$	198.4	127.7	$59.6 \pm$
	19.4	21.0	15.0	9.6	21.0	36.0	155.6			63.5
$[HCO_3^-]$	$153.1\pm$	$189.8 \pm$	$182.8 \pm$	563.9	$350.8 \pm$	$348.4 \pm$	$854.1 \pm$	563.9	_	$287.0 \pm$
	137.0	91.1	86.9		102.8	95.9	252.7			212.1
[Cl <sup>-</sup> ]	$158.3\pm$	$126.5\pm$	$135.2\pm$	$147.9\pm$	$180.3 \pm$	$112.7\pm$	$169.0\pm$	84.5	22.5	$141.3\pm$
	108.9	68.9	63.7	10.0	88.2	23.0	39.8			79.7
[Na <sup>+</sup> ]	$123.8 \pm$	$124.3\pm$	$137.0\pm$	$167.4\pm$	$124.4\pm$	$67.4\pm$	$104.4\pm$	130.4	39.1	$118.1\pm$
	111.8	83.5	52.3	3.1	51.4	94.4	12.3			83.4
$[K^+]$	$23.2\pm$	$21.8\pm$	$25.4\pm$	$36.4\pm$	$25.0\pm$	$21.2\pm$	$43.7\pm$	56.4	18.0	$25.4\pm$
	5.8	3.3	4.0	4.4	1.4	6.9	2.0			8.6
[Ca <sup>2+</sup> ]	$345.8 \pm$	$278.5 \pm$	$376.2\pm$	$1661.2\pm$	$465.7 \pm$	$662.5\pm$	$1850.0\pm$	655.0	210.0	$527.0 \pm$
	267.9	181.7	284.6	723.0	96.3	379.4	495.0			506.4
[Mg <sup>2+</sup> ]	$33.0\pm$	$32.9\pm$	$45.8\pm$	$79.2\pm$	$35.7\pm$	$33.3\pm$	$76.7\pm$	100.0	45.0	$40.7\pm$
	27.2	17.9	8.2	17.7	14.7	34.0	21.2			26.6

**Table 2** Mean monthly and annual figures of pH, total acidity ( $\mu eq l^{-1}$ ), conductivity ( $\mu S cm^{-1}$ ) and concentrations of major anions and cations ( $\mu eq l^{-1}$ ), along with the corresponding standard deviations, in the collected rainwater samples at Heraklio, Attica and at University Campus of Athens

The conductivity of all analyzed samples estimated  $63.4\pm42.0 \ \mu\text{S cm}^{-1}$  for University Campus and  $88.4\pm60.4 \ \mu\text{S cm}^{-1}$  for Heraklio, (Table 1). The conductivity is positively correlated (r=0.67, p<0.05) with pH, concerning the total of rain samples for the two cites (Fig. 3). This relationship is expressed by the linear model: y=-498.8 + 77.8 x and it can be attributed to the neutralization of acids in the rain by ammonia (from fertilizers), marine water and dust from the ground. Neutral rains in Athens must be caused by the counteraction of artificially and naturally acidified rains with calcium carbonate in the dust carried not only from the urban area of Athens by local winds but from arid areas in the world by global atmospheric currents, as well (Kita et al. 2004).

**Table 3** The ratios of mean annual concentrations of major ions  $CI^-$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $[SO_4^{2-}]$  to  $Na^+$ , in the rainwater samples and seawater

Ions ratio	Rainwater samples	Seawater (Galloway et al. 1983)		
[Cl <sup>-</sup> ]/[Na <sup>+</sup> ]	1.19	1.16		
[K <sup>+</sup> ]/[Na <sup>+</sup> ]	0.22	0.02		
[Mg <sup>2+</sup> ]/[Na <sup>+</sup> ]	0.34	0.23		
[Ca <sup>2+</sup> ]/[Na <sup>+</sup> ]	4.46	0.04		
$\left[SO_4^{2-}\right]/[Na^+]$	2.09	0.12		



Fig. 4 Annual march of the surface concentrations (mg  $m^{-2}$  month<sup>-1</sup>) for the elements S, N, Cl, Na, K, Ca and Mg, for the two sampling locations



**Fig. 5** Forty-eight hours air mass back trajectories for the height 1500 m (~850 hPa) ending at the following specific time and dates. The numbers stand for the corresponding rain event and the letter in parenthesis defines the sector (N for North, S for South, W for West, E for East and L for Local): #1(N) at 07 UTC, 03 November 2001; #2(E) at 08 UTC, 04 November 2001; #3(N) at 22 UTC, 05 November 2001; #4(L) at 17 UTC, 19 November 2001; #5(S) at 01 UTC, 20 November 2001; #6(W) at 08 UTC, 23 November 2001; #7(W) at 09 UTC, 24 November 2001; #8(S) at 20 UTC, 28 November 2001; #9(N) at 12 UTC, 01 December 2001; #10(N) at 22 UTC, 02 December 2001; #11(N) at 22 UTC, 07 December 2001; #12(N) at 05 UTC, 09 December 2001; #13(N) at 07 UTC, 13 December 2001; #14(S) at 05 UTC, 16 December 2001; #15(N) at 06 UTC, 21 December 2002; #19(S) at 23 UTC, 10 March 2002; #20(N) at 22 UTC, 15 March 2002; #21(N) at 04 UTC, 16 March 2002; #22(L) at 00 UTC, 16 April 2002; #26(W) at 04 UTC, 30 August 2002

Another parameter that was calculated is the total acidity of rain  $[H^+]_{Total}$  (Galloway et al. 1983):

$$\left[\mathrm{H}^{+}\right]_{\mathrm{Total}} = \left[\mathrm{H}^{+}\right]_{\mathrm{pH}} + \left[\mathrm{Alk}\right]_{\mathrm{ss}}$$

where  $[H^+]_{pH}$  represents the free acidity of rain  $([H^+]_{pH}=10^{-pH})$  and  $[Alk]_{ss}$  is the alkalinity from the marine salt and is given by the formula:

$$[Alk]_{ss} = 0.00484 [Na^+]ppt$$

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Section	Cases	pН	Conductivity	$\mathrm{SO_4}^{2-}$	$NO_3^-$	$\mathrm{HCO}_3^-$	$Cl^-$	$Na^+$	$K^+$	$\mathrm{Ca}^{2+}$	Mg <sup>2+</sup>
North	16	7.2	55.4	173.2	45.2	212.6	121.7	108.1	24.2	342.5	34.1
South	11	7.6	84.6	204.2	48.4	298.6	135.0	112.8	25.2	462.1	38.0
Local	5	7.3	91.6	370.8	59.5	218.9	156.1	136.2	25.6	724.3	44.7
West	5	7.6	125.4	483.3	144.8	706.0	205.1	183.3	33.0	1073.5	73.0
East	2	7.6	48.0	145.8	24.2	344.3	126.8	19.6	16.7	500.0	16.7

**Table 4** pH, conductivity ( $\mu$ S cm<sup>-1</sup>) and mean concentrations of major anions and cations ( $\mu$ eq l<sup>-1</sup>), for every section estimated from air mass trajectories analysis

where  $[Na^+]_{ppt}$  is the sodium concentration in the rain samples expressed in (µeq  $l^{-1}$ ). The figures of total acidity range from 0.2 to 2.0 (µeq  $l^{-1}$ ).

Table 2 presents the mean monthly and annual figures of pH, total acidity ( $\mu$ eq l<sup>-1</sup>), conductivity ( $\mu$ S cm<sup>-1</sup>) and concentrations of major anions and cations ( $\mu$ eq l<sup>-1</sup>), with the corresponding standard deviation, for the total of the rain samples during the investigated period (September 2001–August 2002).

As it was mentioned before, neutral or even alkaline pH figures show that the main process in the rain is the neutralization. The ratio of the mean annual concentrations (for 39 samples) of chloride to sodium (Table 3) is 1.19, and this compared to the corresponding ratio 1.16 existed in marine water (Galloway et al. 1983), drives to a conclusion that the chemical composition of rain is influenced more by the sea. Besides, the marine origin of magnesium and sodium ions is proved by their ratio, which is 0.34, (0.23 in marine water). Taking into consideration the ratios of ions determined in the rain samples and in the seawater (Galloway et al. 1983), it is obvious that the marine water is the main source for the Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>, while the origin of the ions K<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> is associated with other sources. Also, the results of the analysis showed that the concentration of SO<sub>4</sub><sup>2-</sup> ions exceeded the concentration of NO<sub>3</sub><sup>-</sup> ions in all samples and their ratio [SO<sub>4</sub><sup>2-</sup>]/[NO<sub>3</sub><sup>-</sup>] in the rain was calculated equal to 4.14. This finding is in agreement with Tsikritsis (2006), who concluded that rainwater acidity in Larissa (Greece) is mainly due to H<sub>2</sub>SO<sub>4</sub> and secondary to HNO<sub>3</sub>.

Figure 4 depicts the annual course of surface concentrations (mg m<sup>-2</sup> month<sup>-1</sup>) for sulphur, nitrogen, chloride, sodium, potassium, calcium and magnesium for both the two sampling locations. It is remarkable that a very high concentration of the aforementioned elements is evident during July, very likely due to the accumulation of pollutants in the

dings or analysis on of the axes		Factors					
		1	2	3			
	$[SO_4^{2-}]$	0.8					
	$[NO_3^-]$	0.8					
	$[HCO_3^-]$		0.8				
	Cl <sup>-</sup>			0.9			
	Na <sup>+</sup>			0.8			
	$K^+$	0.9					
	Ca <sup>2+</sup>		0.7				
	$Mg^{2+}$	0.8		0.6			
	pН		0.9				

 Table 5
 Factor loadings

 extracted from factor analysis

 with varimax rotation of the axes



Fig. 6 Scatter plot of rain sample factor scores, derived by Factor analysis, for the sectors extracted by air mass back trajectories

atmosphere combined with the absence of rainfalls for a long time period before. Another explanation is the transboundary air pollution which is driven by the northeastern flow of the Etesian winds established in the Aegean sea during summer time. According to O'Sullivan (1989) the percentage of sulphur deposition in Greece from other countries is 63%.

Further to, the effect of the origin of air masses on the configuration of the chemical composition of rain is investigated. For this reason, the 48 hours air mass back trajectories for the 26 different days of sample collection were calculated, using the HYSPLIT 4 model of Air Resources Laboratory of NOAA and are depicted in Fig. 5. Two different levels were used: 1500 and 3000 m (~850 and 700 hPa, respectively). In 9 cases the air masses come from different directions in the two examined trajectory heights. Based on the results of the air masses back trajectories analysis we distinguished 5 sectors according to the origin of the air masses. Trajectories coming from the north (NW–NE Europe) consist the northern sector (N), from Northern Africa, the southern sector (S), from the grid box defined by the coordinates 18°–28° E, 35°–42° N, the local sector (L), from the Western Mediterranean, the western sector (W) and finally from the Asia Minor and Cyprus, the eastern sector (E). If the trajectory remained within the mentioned grid box for 48 hours it was characterized as local.

The mean chemical concentration for each sector, calculated by the air masses back trajectory analysis, is appeared in Table 4. We observe low mean ions concentrations with respect to the northern sector and high to the western sector, while intermediate concentrations are associated with the southern and local sectors. Regarding the eastern



Fig. 7 Scatter plot of rain sample discriminant scores, derived by discriminant analysis

sector, the concentrations of the ions  $NO_3^-$ ,  $Na^+$ ,  $K^+$  and  $Mg^{2+}$  present the smallest figures from all the other sectors, while pH and conductivity are lower in the northern sector.

In the process, FA with varimax rotation of the axes was applied, to the  $\log_{10}$  converted data and three main factors (eigenvalue  $\geq 1$ ) were extracted, which explain 90% of the total variance, (Table 5). The first main factor that interprets 61% of the total variance is strongly associated with the ions  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $K^+$  and  $Mg^{2+}$ , and implies mainly the anthropogenic contribution. The second factor (17%) comprises the ions  $HCO_3^{-}$ ,  $Ca^{2+}$  and pH and for this reason represents the alkalinity–acidity factor. The third factor (12%) is strongly correlated with the ions  $CI^-$  and  $Na^+$ , as well as moderately correlated with  $Mg^{2+}$  and stands for the marine origin of pollutants. Similar conclusions are reported in the study of Glavas and Moschonas (2002).

The plot of factor scores (the coefficients of each rain sample within each extracted main factor) of each rain sample, classified to sectors according to the back trajectories analysis is depicted in Fig. 6. The ordinate of the graph represents the anthropogenic factor, which explains 61% of the total variance while the abscissa is the acidity–alkalinity factor, accounted for 17% of the total variance. The north sector is well distinguished from the other sectors along the acidity–alkalinity axis.

Better results are taken out by the application of DA on the factor scores extracted by the FA. Discriminant function 1 accounted for 75.5% of the total variance is strongly correlated with acidity–alkalinity, discriminant function 2 accounted for 18.2% of the total variance is strongly correlated with the ions due to anthropogenic activities and discriminant function 3 accounted for 6.3% is also strongly correlated with ions influenced by marine origin. Figure 7 exhibits the results regarding the first two out of three discriminant functions extracted. The first function (75.5%) is the abscissa and represents the acidity–alkalinity while the second function (18.2%) is the ordinate and stand for the anthropogenic activities.

Four groups distinguished by the same symbols as in Fig. 6 correspond to the sectors obtained by the air masses trajectory analysis. The east sector is not appeared in the graphs because of its small contribution (only two rain samples). The northern and southern sectors present the greater dispersion along the axis of alkalinity–acidity. The southern and local sectors are depicted between the northern and the western sector, as they were expected, accordingly to the trajectory analysis of the air masses. (Table 4).

### 4 Conclusions

The application of multivariate analysis to the concentrations of major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and cations (H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) showed that the chemical composition of rain in Athens is determined by three main factors, which explain 90% of the total variance. The first factor (61%) is associated with the ions  $SO_4^{2-}$ , NO<sub>3</sub><sup>-</sup>, K<sup>+</sup> and Mg<sup>2+</sup>, and implies mainly the anthropogenic contribution. The second factor (17%) is correlated with the ions  $HCO_3^-$ ,  $Ca^{2+}$  and the pH and for this reason is the so-called alkalinity–acidity. The third factor (12%) is correlated with the ions Cl<sup>-</sup> and Na<sup>+</sup>, as well as Mg<sup>2+</sup> and represents the marine origin of pollutants. Another finding of our research is that the frequency distribution reveals a shift towards alkalinity in the rain sample from the previous year to the year of our study. Finally, the back trajectories analysis showed that the air masses coming from NW–NE Europe (northern sector) are associated with less ion concentrations in the rain water, while Western Mediterranean (western sector) is responsible for more ion concentrations.

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