WET DEPOSITION IN TWO GREEK SITES: LARISSA AND ATHENS

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Presented at the 14th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region (MESAEP), Sevilla, Spain, 10 – 14 Oct. 2007

ABSTRACT

The determination of the chemical composition of rainfall related to the origin of the air masses, in two urban sites in Greece during the year 2006, is investigated in this study. Two model automatic rain samplers were installed, the first in the city of Larissa, Thessaly, central Greece and the second in Heraklio, Attica, a northern suburb of Athens. The concentrations (ppm) of the major cations (H^+, Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+}) and major anions (NO_3^-, NO_2^-, HCO_3^-, and SO_4^{2-}), as well as total hardness (ppm $CaCO_3$), pH and electric conductivity in 25 ^oC (μS/cm) for 27 rainfall samples -11 samples in Larissa and 16 samples in Heraklio (Athens)- were determined.

In Larissa, the figures of pH range from 5.13 to 6.13 while in Heraklio (Athens), the pH within the range 5.62 to 7.88 indicates a shift of the rainfalls towards alkalinity. The electric conductivity in Larissa ranges from 16.30 μS/cm to 110.60 μS/cm and in Heraklio (Athens) from 7.00 μS/cm to 151.00 μS/cm. The analysis showed that Ca^{2+} and Mg^{2+} appear the highest concentrations out of the examined cations, while HCO_3^- and SO_4^{2-} present the highest concentrations within the anions. Moreover, in order to find out the origin of the air masses, the air mass back trajectories were calculated using the HYSPLIT 4 model of Air Resources Laboratory of NOAA for two different levels: 1500 and 3000 m (a.m.s.l.).

KEYWORDS: Wet deposition, air mass back trajectories, Athens, Larissa, Greece.

INTRODUCTION

Acid rain is responsible for many environmental problems, such as impacts on the life in the water as well as the life on land. It is almost worse in water than on land because the fish that are in the water need the water to breathe. Trees are also harmed by acid rain. The atmosphere deposits a lot of toxic metals into the forests because acid rain contains metal, such as lead, zinc, copper, chromium, and aluminium. The main components that produce acid rain are the sulphur dioxide (SO_2) and the nitrogen oxides (NO_x). These ambient air pollutants are emitted by natural and human activities. A lot of studies and analyses have been carried out concerning the emissions and deposition of air pollutants which cause acid rain [1-3]. In the central-eastern Mediterranean, acid episodes (pH<5), and a great percentage of episodes with pH>6 appeared [4-9]. In Greece, the phenomenon of acid rain has been studied since approximately 25 years ago in order that the reasons responsible for the observed deterioration of the marbles of Parthenon are revealed [10-12]. Later on, a lot of researchers studied systematically the phenomenon of acid rain during different time periods in Athens [5, 13-18], in Thessalonica [6], in Patras [4, 19], in Crete [20] and in central Greece [21].

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 Greek cities: the city of Larissa (LAR) and the city of Heraklio (HER), Attica, a northern suburb of Athens, during 2006. The objective of the analysis is to find out the possible differentiations in the chemical composition of the rainfall in the two sites and make an effort to interpret these, using the air mass back trajectories analysis.

DATA AND ANALYSIS

The data analyzed concern the concentrations (ppm) of the major cations (H^+, Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+}) and major anions (NO_3^-, NO_2^-, HCO_3^-, and SO_4^{2-}), as well total

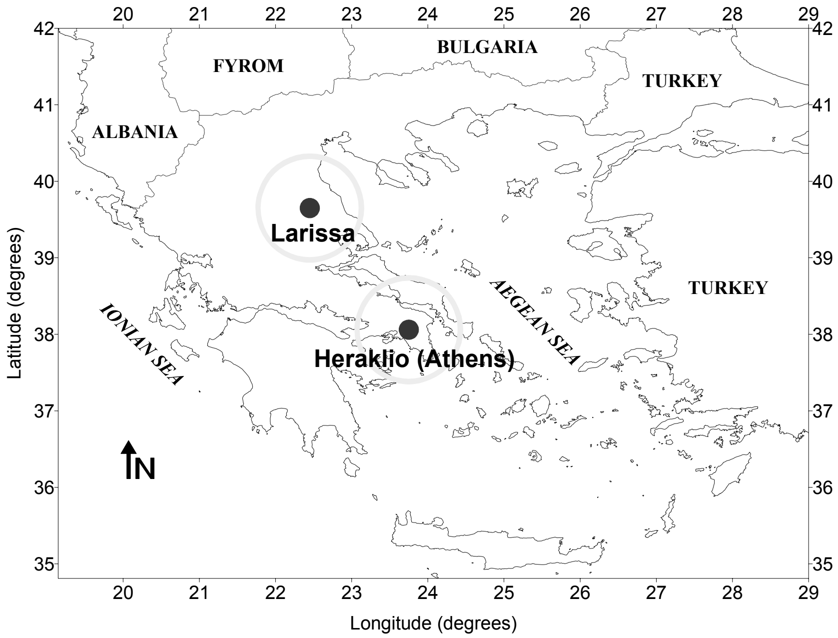

FIGURE 1 - Locations of the two sampling sites.

hardness (ppm $CaCO_3$), pH and electric conductivity in 25 ^oC (μS/cm) for 27 rainfall samples collected in LAR (11 samples), a city in central Greece (lowland and medium-sized city with a population of about 150.000 inhabitants according to the census of 2001) and in HER (16 samples), a northern suburb of Athens (population of about 46.000 inhabitants according to the census of 2001). Regarding the samples collected in HER, all the16 samples were taking into consideration for the determination of pH and conductivity, but only 6 samples analyzed for the estimation of major anions and cations, because of the analysis limitations arised due to less rainfall volume collected. The number of samples collected is relatively small due to precipitation scarcity, which is likely driven by the climatic change in the Southeastern Mediterranean region. Notwithstanding, the results obtained are representative for the chemical composition of the wet deposition in the two sites examined. The rainwater sampling was achieved by two automatic rain samplers [5, 13], established in the two sites, during 2006 (Figure 1). The rainwater samples were collected in 24-h basis.

The samples were collected in polyethylene bottles [22] of one litre, and were promoted in the chemical laboratory for the analyses. The conductivity and pH were measured at once after the sample collection. The conductivity meter (WTW 3L5i) and the pH meter (Metrohm 744) were calibrated 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 Millipore 0.45 μm pore size membrane filters, aiming in the removal of suspended solids. The determination of anions NO_3^-, NO_2^-, SO_4^{2-} and cations NH_4^+, was carried out using a Hitachi 1100 (UV-Vis) spectrophotometer, while HCO_3^-, Ca^{2+} and Mg^{2+} ions were measured using a Hach alkalinity titrator. In the process, Na^+ και K^+ ions were specified using a flame photometer (Jenway PFP 7). Total hardness (permanent and transitory) values were calculated as follows: Total Hardness (ppm $CaCO_3$) = meq/L (calcium + magnesium) x 50; Temporary Hardness (ppm $CaCO_3$) = meq/L (carbonate + bicarbonate) x 50; Permanent Hardness = Total Hardness – Transitory Hardness.

For the calculation of the back trajectories, the HYSPLIT-4 model of Air Resources Laboratory of NOAA [23, 24] is used for two different levels: 1500 and 3000 m (a.m.s.l.).

RESULTS AND DISCUSSION

The concentration of CO_2 in the atmosphere is approximately 325 ppm CO_2, which corresponds to a typical pH value of approximately 5.6. With respect to the examined period, episodes of acid rain (pH<5.6) account for 36% of the total events analyzed in LAR, while these are not observed in HER (Figure 2). In Larissa, the figures of pH range from 5.13 to 6.13 with mean ± SD value: 5.64 ± 0.30, while in HER the pHs mean value ± SD (6.32 ± 0.54) within the range 5.62 to 7.88 indicates a shift of the rainfalls towards alkalinity. The frequency distribution of pH shows that the class 5.5-6.0 is the prevailing one (55%) for LAR, while the class 6.0-6.5 (38%) dominates in the case of HER.

Notwithstanding, results from previous studied period (1/9/2001-31/8/2002) revealed that, the class 7.5-8.0

presented the highest frequency; 38% for HER [18], while in the present study the class 7.5-8.0 accounts for 6%. A possible explanation is that the numerous worksites established in the Greater Athens Area (GAA), concerning the Olympic constructions of the 2004 Olympic Games, emitted a lot of dust and particulate matter resulted in the alkalinity of the rainfalls. Kita et al. [16] suggested that 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.

The conductivity in Larissa ranges from 16.30 μS/cm to 110.60 μS/cm with mean value ± SD: 35.38 ± 25.35 μS/cm and in HER from 7.00 μS/cm to 151.00 μS/cm with mean value ± SD: 42.81 ± 37.48 μS/cm. With respect to conductivity histograms (Figure 2), we observe that the class 0-40 μS/cm is the most prevailing in both examined sites. Nevertheless, high conductivity values (120-160 μS/cm) appear in HER, which combined to the observed high pH values (7.5-8.0) leads to the assumption that neutralization is a likely process, taking part in the GAA.

The conductivity is positively correlated with pH, concerning the total of rain samples for the two sites; LAR: r=0.6, p<0.042 and HER: r=0.7, p<0.003 (Figure 3). These relationships are expressed by the linear regression models: y=-263.2+52.9x for the sampling site in LAR and y=-259.3+47.8x for the site in HER and could be attributed to the neutralization of acids in the rain by ammonia (from fertilizers), marine water and dust from the ground.

Furthermore, the results of the analysis showed that the concentration of SO_4^{2-} ions is higher than the concentration of NO_3^- ions in all samples and their ratio $[SO_4^{2-}]/[NO_3^-]$ in the rain was calculated equal to 4.71 for LAR and 2.38 for HER. These findings are in agreement with Tsikritsis [21] and Nastos et al. [18] respectively, who concluded that rainwater acidity in LAR and HER is mainly due to H_2SO_4 and secondary to HNO_3. Figure 4 depicts the calculated concentrations (ppm) of the NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} ions for the two sampling sites. It is crystal clear the predominance of SO_4^{2-} anions compared to NO_3^- anions, especially in LAR. Besides, Ca^{2+} cations prevail against Mg^{2+} cations in LAR, while this pattern is reversed in HER. Regarding the NO_2^- anions, we found that their concentrations are by far higher in LAR (mean=0.12 ppm) than HER (mean=0.009 ppm) and this could be attributed to the agricultural activities taking place in LAR. Low concentrations with respect to K^+ cations (LAR: mean=0.07 ppm; HER: mean= 0.56 ppm), NH_4^+ cations (LAR: mean=0.12 ppm; HER: mean=0.32 ppm) were measured in the rainwater

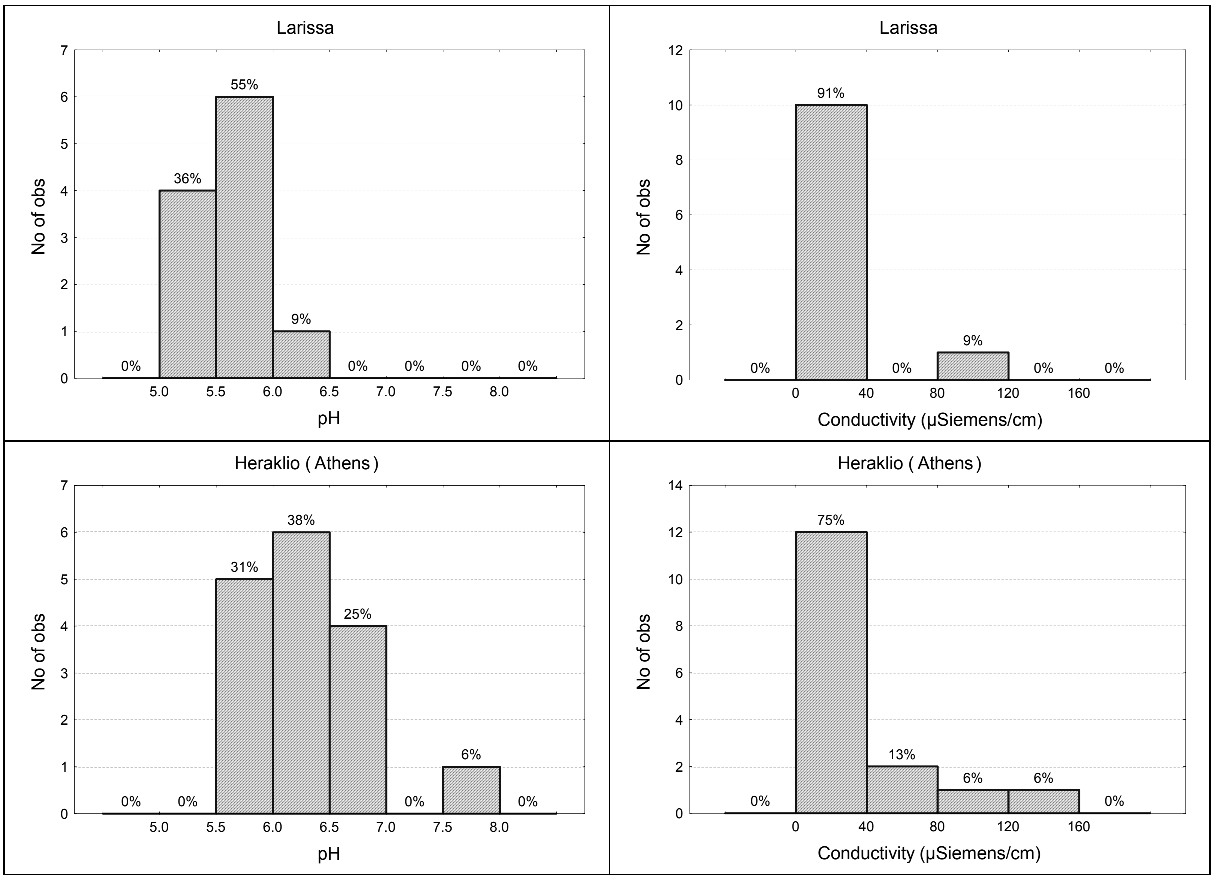

FIGURE 2 - Histograms of pH and conductivity for the two sampling sites.

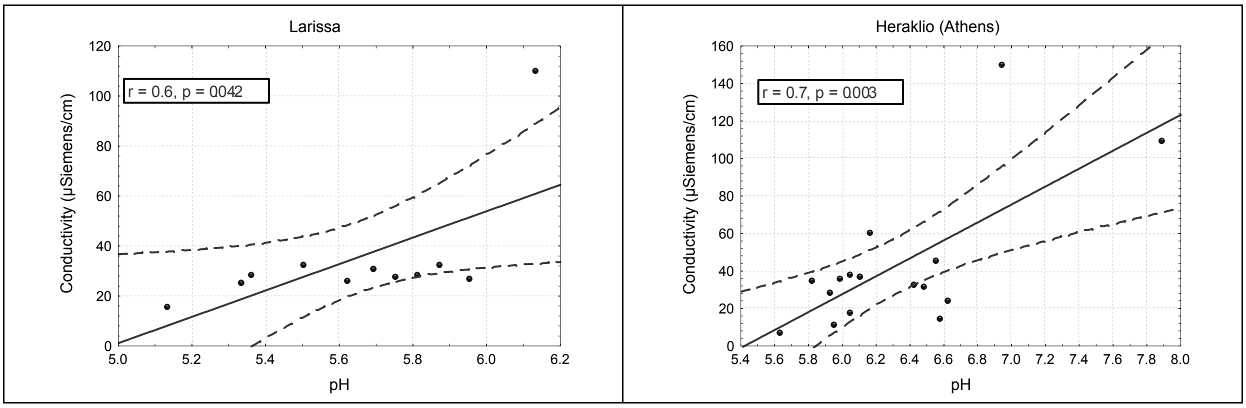

FIGURE 3 - Conductivity as a function of pH for the two sampling sites.

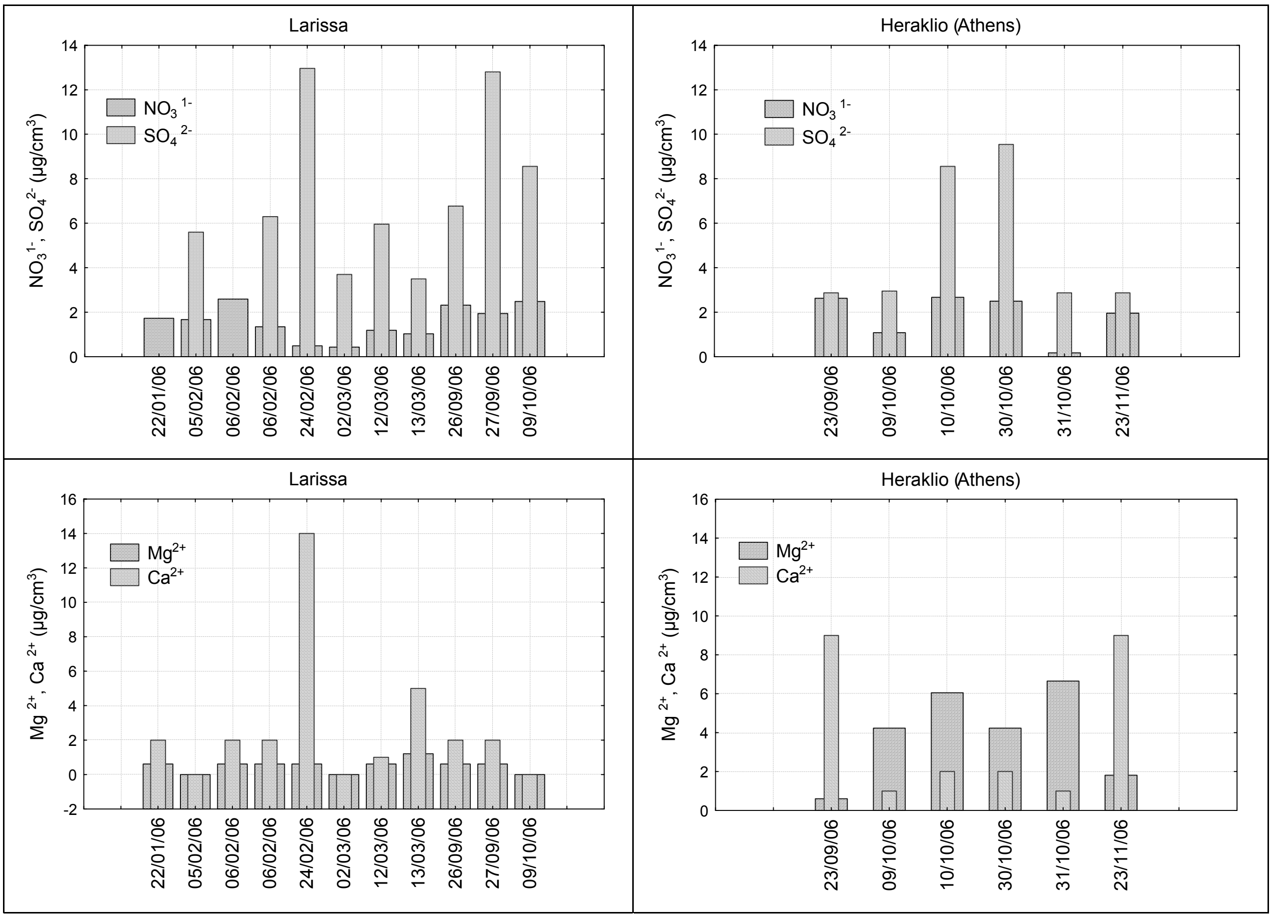

FIGURE 4 - NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} concentrations (ppm) for the two sampling sites.

samples, while Na^+ cations were not measured in the water samples of both sites. The total hardness is strongly correlated ($r>0.9$, $p<0.05$) with HCO_3^- ions (LAR: mean=20.24 ppm; HER: mean=83.37 ppm) with higher values appeared in HER (mean=68.33 ppm) than LAR (mean=17.05). It is considerable to remark that high ions concentrations were evaluated during light rain events and after preceding dry periods. The wash out effect of the ambient air pollutants is more effective during low intensity rains [6].

In the process, 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 rainy events were calculated, using the HYSPLIT-4 model of Air Resources Laboratory of NOAA and are depicted in Figure 5. Two different levels were used: 1500 and 3000 m (~850 and 700 hPa, respectively). The air masses come from different directions in the two examined trajectory heights for approximately half cases concerning both sampling sites. The sectors according to the origin of air masses were distinguished as follows: 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 Kaspian Sea, the eastern sector (E). If the trajectory remained within the mentioned grid box for 48 hours it was characterized as local.

The air mass back trajectories analysis revealed the variability of the mean concentrations of the major anions and cations (ppm), among sectors (Table 1). In LAR, the air masses coming from the northern sector decrease pH and as a consequence the concentration of H^+ ions is the highest from all other sectors. The conductivity and pH present maximum values within the southern sector due likely to high concentrations of HCO_3^-, SO_4^{2-}, Ca^{2+} ions and the total hardness. The high figures of pH, conductivity, total hardness, HCO_3^- and Ca^{2+} ions might be associated with Saharan dust events, mainly appear in spring. Saharan dust is reported as the source of alkaline earths in several Mediterranean places [7, 25]. The local sector results in high concentrations of NO_3^- and NO_2^- ions and this probably be attributed to the lignite mines in Ptolemais, Northern Greece, used for electricity production, which are established at the NW of Larissa.

In HER, air masses from the southern sector contribute in high conductivity, high concentrations of HCO_3^- and Ca^{2-} ions, as well as high total hardness. This is due to a Saharan dust event, as it is depicted in Figure 7. Kosmopoulos et al. [26] evaluated the seasonal variability of specific aerosol types over GAA, analyzing a long-term (2000-2005) data set of aerosol optical properties obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) over the GAA. The Desert Dust (DD) type exhibited its higher frequency in summer, when the atmospheric conditions favor the erosion of soil dust from the dry surfaces, the more stable atmospheric conditions and the absence of precipitation; all these mechanisms allow aerosols to suspend in the air.

On the other hand, the aerosol load and optical properties of the DD type were strongly related to the air mass pathways and natural events (e.g., Sahara dust transport over the study region), exhibiting significant variability from year-to-year. The Aerosol Optical Depth at 550nm (AOD_{550}) for this aerosol type was higher in spring due to the more intense dust events occurring in this period. Particularly high AOD_{550} values were also observed in winter, despite the very low occurrence of DD type in this season. However, the occurrence of the DD type in winter was closely associated with air masses coming from Sahara.

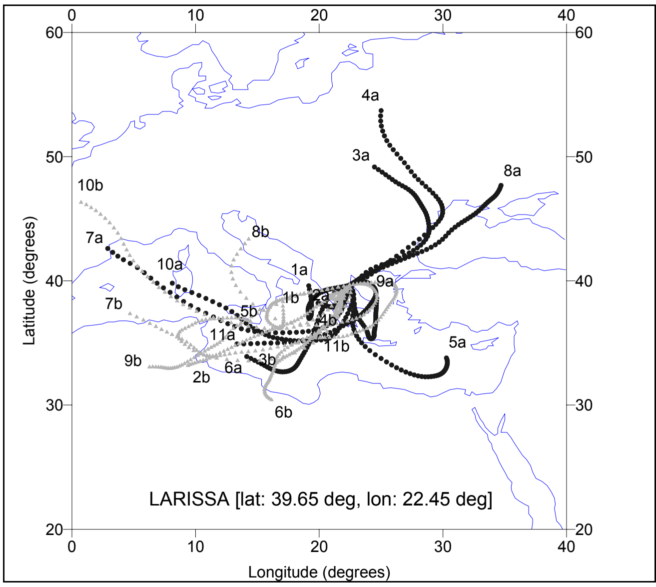

FIGURE 5 - 48 hours air mass back trajectories for the heights: 1500 m (~850 hPa) and 3000 m (~700 hPa), ending at the following specific time and dates for Larissa: Black trajectories (circles) for the height of 1500 m (a) while grey trajectories (triangles) for the height of 3000 m (b). The numbers stand for the corresponding rain event : #1 at 04 UTC, 22 January 2006; #2 at 07 UTC, 05 February 2006; #3 at 04 UTC, 06 February 2006; #4 at 17 UTC, 06 February 2006; #5 at 13 UTC, 24 February 2006; #6 at 18 UTC, 02 March 2006; #7 at 13 UTC, 12 March 2006; #8 at 17 UTC, 13 March 2006; #9 at 18 UTC, 26 September 2006; #10 at 14 UTC, 27 September 2006; #11 at 17 UTC, 09 October 2006.

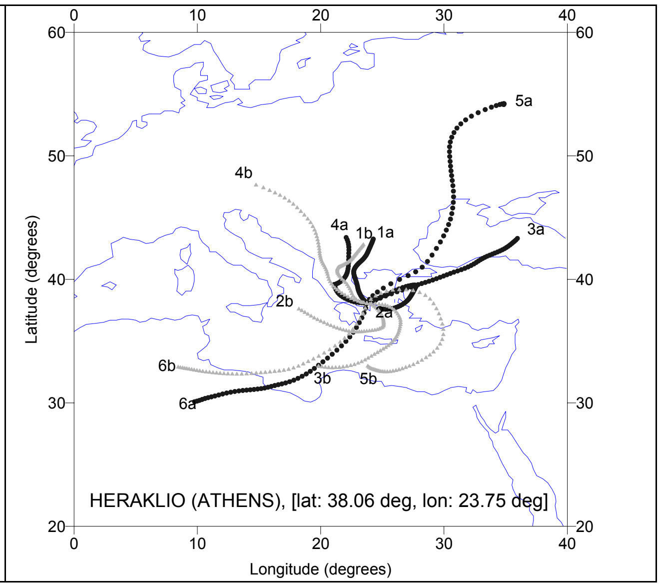

FIGURE 6 - 48 hours air mass back trajectories for the heights: 1500 m (~850 hPa) and 3000 m (~700 hPa), ending at the following specific time and dates for Athens: Black trajectories (circles) for the height of 1500 m (a) while grey trajectories (triangles) for the height of 3000 m (b). The numbers stand for the corresponding rain event: #1 at 01 UTC, 23 September 2006; #2 at 16 UTC, 09 October 2006; #3 at 22 UTC, 10 October 2006; #4 at 09 UTC, 30 October 2006; #5 at 22 UTC, 31 October 2006; #6 at 21 UTC, 23 November 2006.

TABLE 1 - pH, conductivity (μS cm^{-1}) and mean concentrations of major anions and cations (ppm), for every sector estimated from air mass back trajectories analysis, for Larissa and Heraklio (Athens).

Larissa												
Sectors	pH	H^+	Conductivity	NO_3^-	NO_2^-	HCO_3^-	SO_4^{-2}	Ca^{+2}	Mg^{+2}	K^+	NH_4^+	Total Hardness
North	5.52	3.19	30.97	1.66	0.100	18.30	4.90	3.00	0.81	0.04	0.08	15.83
South	6.00	1.04	71.8	0.46	0.100	32.02	8.33	7.00	0.30	0.08	0.06	27.50
Local	5.75	1.78	28.4	2.32	0.030	18.30	6.77	2.00	0.61	0.10	0.09	15.00
West	5.79	1.69	27.47	1.87	0.146	18.30	9.11	1.00	0.41	0.11	0.17	15.00
East	----	----	----	----	----	----	----	----	----	----	----	----
Heraklio (Athens)												
Sectors	pH	H^+	Conductivity	NO_3^-	NO_2^-	HCO_3^-	SO_4^{-2}	Ca^{+2}	Mg^{+2}	K^+	NH_4^+	Total Hardness
North	6.16	0.82	21.00	1.77	0.004	61.00	5.09	4.00	3.83	0.53	----	50.00
South	6.10	0.79	37.00	1.96	0.011	183.00	2.87	9.00	1.82	----	0.17	150.00
Local	5.62	2.40	7.00	1.08	0.004	73.2	2.95	1.00	4.23	0.30	0.21	60.00
West	----	----	----	----	----	----	----	----	----	----	----	----
East	5.82	1.51	35.00	2.67	0.006	61.00	8.56	2.00	6.05	0.60	0.59	50.00

The local sector is related to low pH and high concentration of H^+ ions. As expected, in an urban environment, like Athens, the Urban Industrial (UI) aerosol type clearly dominates against the DD type. The UI type occurred mainly in spring, directly related to the intensity of anthropogenic emissions, stagnant air masses and poor dilution of aerosols and pollutants in rain [26]. Another important finding of the performed back trajectories analysis is that, high concentrations of approximately the total examined ions were associated with air masses coming from the eastern sector (Table 1).

CONCLUSIONS

The analysis showed that in both examined sites, Larissa and Heraklio (Athens), air masses coming from the southern sector contribute in the neutralization of acids in the rain by marine water and Saharan dust. On the other hand, the local and eastern sector for Heraklio (Athens) is related to high concentrations of almost all the major ions in the rainwater, while the local and western sectors for Larissa play an important role in the enrichment of the rainwater with high concentrations of NO_3^-, NO_2^- and SO_4^{2-} ions. Moreover, Ca^{2+} ions prevail from the cations in all samples collected in Larissa while Mg^{2+} ions and secondary Ca^{2+} ions are abundant in Heraklio (Athens); HCO_3^- and SO_4^{2-} present the highest concentrations within the anions. Besides, our findings indicate that rainwater acidity in Larissa and Heraklio (Athens) is mainly due to H_2SO_4 and secondary to HNO_3.

ACKNOWLEDGEMENTS

This study is co-funded by the European Social fund and National Resources – EPEAEK II (ARCHIMEDES II).

REFERENCES

[1] Beilke, P. (1983) Acid deposition. The present situation in Europe. Technical Report EUR 8307, Comm. Eur. Communities, 3-30.

[2] CEC (1985) Report on the actions of the Commission of the EEC on acid deposition. EUR 9985 EN, 1-57.

[3] Pierson, W.R. and Chang, T.Y. (1986) Acid rain in Western Europe and Northeastern United States- Technical appraisal. Critical Reviews in Environmental Control, 16, 167-192.

[4] Glavas, S. (1988) A wet only precipitation study in a Mediterranean site, Patras, Greece. Atmospheric Environment, 22, 1505-1507.

[5] Dikaiakos, I.G., Tsitouris, C.G., Siskos, P.A, Melissos, D.A. and Nastos, P.T. (1990) Rainwater Composition in Athens, Greece. Atmospheric Environment, 24B, 171-176.

[6] Samara, C., Tsitouridou, R. and Balafoutis, Ch. (1992) Chemical Composition of Rain in Thessaloniki, Greece, in relation to Meteorological Conditions. Atmospheric Environment, 26B, 359-367.

[7] LeBolloch, O. and Guerzoni P. (1995) Acid and alkaline deposition in precipitation on the western coast of Sardinia, central Mediterranean. Water, Air and Soil Pollution, 85, 2155-2160.

[8] Tuncel, P.G. and Ungoer, P. (1996) Rain water chemistry in Ankara, Turkey. Atmospheric Environment, 26B, 483-490.

[9] Guelsoy, G., Tayanc, M. and Ertuerk, F. (1999) Chemical analysis of the major ions in the precipitation of Instanbul, Turkey. Environmental Pollution, 105, 273-280.

[10] Vocom, I.E. (1979) Air pollution damage to buildings on the Acropolis. Journal of Air Pollution and Control Association, 29, 333-338.

[11] Skoulikidis, T.N. (1983) Effects of primary and secondary air pollutants and acid depositions on (ancient and modern) buildings and monuments. In: Proceedings of the EEC Symposium: “Acid deposition. A Challenge for Europe”. Karlsruhe, 193-226.

[12] Cheng, R.I., Hwu, I.R., Kim, J.T. and Leu, P.M. (1987) Deterioration of marble structures. The role of acid rain. Analytical Chemistry, 59, 104A-106A.

[13] Dikaiakos, J.G. and Nastos, P.T. (1987) Chemical analysis of rain in Athens. Publication of the Laboratory of Climatology and Atmospheric Environment, University of Athens, No 23.

[14] Smirnioudi, V.N. and Siskos, P.A. (1992) Chemical Composition of Wet and Dust Deposition in Athens, Greece. Atmospheric Environment, 26B, 483-490.

[15] Kelepertsis, A.E., Nastos, P.T., Alexakis, D.E. and Kanellopoulou, E.A. (2002) Chemical analysis of rain in Athens. In: Proceedings of the 6th Hellenic Congress in Meteorology, Climatology and Atmospheric Physics, Ioannina, Greece, 122-131.

[16] Kita, I., Sato, T., Kase, Y. and Mitropoulos, P. (2004) Neutral rains at Athens, Greece: a natural safeguard against acidification of rains. Science of the Total Environment, 327, 285-294.

[17] Nastos, P.T., Alexakis, D., Kanellopoulou, E.A. and Kelepertsis, A.E. (2004) Chemical composition of rainwater in Athens, in relation to the pollutants sources. In: Proceedings of the 7th Hellenic Scientific Congress in Meteorology-Climatology and Atmospheric Physics, Nicosia, Cyprus, 845-855.

[18] Nastos, P.T., Alexakis, D., Kanellopoulou, E.A. and Kelepertsis, A.E. (2007) Chemical composition of wet deposition in Athens, Greece, related to the origin of air masses. Journal of Atmospheric Chemistry, 58, 167-179.

[19] Glavas S. and Moschonas, N. (2002) Origin of observed acidic-alkaline rains in a wet-only precipitation study in a Mediterranean coastal site, Patras, Greece. Atmospheric Environment, 36, 3089-3099.

[20] Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsis, P. and Bousquet, P. (1997) Tropospheric aerosol ionic composition in the Eastern Mediterranean region. Tellus 49B, 314-326.

[21] Tsikritsis, G.E. (2006) Precipitation Chemistry in Central Greece. Fresenius Environmental Bulletin, 15, 1499-1505.

[22] Moody, J.R. and Lindstrom, R.M. (1977) Selection and cleaning of plastic containers for storage of trace element samples. Analytical Chemistry, 49, 2264-2267.

[23] Draxler, R.R. and Hess, G.D. (1997) Description of the HYSPLIT-4 modeling system. NOAA Technical Memorandum ERL ALP-224, p. 24.

[24] Draxler, R.R. and Hess, G.D. (1998) An overview of the HYSPLIT-4 modeling system for trajectories, dispersion and deposition. Australian Meteorological Magazine, 47, 295-308.

[25] Rogora M., Mosello R. and Marchetto A. (2004) Long-term trends in the chemistry of atmospheric deposition in Northwestern Italy: the role of increasing Saharan dust deposition. Tellus B, 56, 426-434.

[26] Kosmopoulos, P.G., Kaskaoutis, D.G., Nastos, P.T., and Kambezidis, H.D. (2007) Seasonal variation of columnar aerosol optical properties over Athens, Greece, based on MODIS data. Remote Sensing of Environment, DOI: 10.1016/j.rse.2007.11.006, article in press.

Received: December 17, 2007
Revised: April 09, 2008
Accepted: June 12, 2008

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FEB/ Vol 17/ No 10a/ 2008 – pages 1648 – 1654