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FOURIER ANALYSIS OF THE MEAN MONTHLY NO_x CONCENTRATIONS IN THE ATHENS BASIN

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ABSTRACT
In the present work, Fourier Analysis is applied to the mean monthly NO_x concentrations of the period 1989-1999, for a network of 7 stations. Treating NO and NO_2 as a single primary pollutant, we succeeded the assessment of NO_x concentrations. The main causes of NO_x emissions in urban areas are the road traffic and the industrial activity.
The annual variation of NO_x concentration is well described with only two harmonic components, which explain over 90% of the total variance. The spatial distribution of the time of maximum, for every one of the two harmonic components in Athens basin, is also presented.

KEYWORDS: Fourier analysis, annual variation, spatial distribution, NO_x concentrations, Athens.

INTRODUCTION
Many researchers have studied the air pollution in Athens or more specifically the creation of urban smog and the influence on the civilians during the last years (Lalas *et al.*, 1983; Mantis *et al.*, 1992; Kallos *et al.*, 1993; Ziomas *et al.*, 1995; Kalabokas *et al.*, 1999 among others). The high population density (3.5 million people in an area of 450 Km^2) along with the anthropogenic activities (automobile traffic, central heating) and the industrial activity contribute to the appearance of the so-called "nephos" in Athens. It is well known that car traffic is responsible for emissions of carbon monoxide, nitrogen oxides, black smoke and hydrocarbons, while industry releases sulfur dioxide and suspended particles. Especially the pri-

Figure 1. Air pollution network in the Athens basin.

vate cars that contribute in car traffic with great percentage have an increase rate of 6% per year (Min. of the Env. Report, 1998). After 1991, that increase concerns only new technology cars with three-way catalyst in their exhausts, but the old technology cars using leaded gasoline were the majority in 1997.

The air pollution episodes appear in Athens, during all the seasons of the year, but the maximum is strongly associated with the development of sea breeze (Kallos *et al.*, 1993). Except the great frequency of sea breeze, the main factors that form air pollution episodes are the local topography with mountains surrounding the basin of Athens and preventing the ventilation of the urban area, the wind flow field, which in the boundary layer is mainly of northeastern direction, during the warm period of the year and the existing sunshine. The last factor is responsible for the transformation of primary pollutants such as nitrogen oxides to photochemical pollutants.

DATA AND ANALYSIS

In this study, Fourier analysis is applied to the mean monthly NO_x concentration timeseries, during the period 1989-1999, for an automated air pollution network of 7 stations (N. SMIRNI[1], PIRAEUS[2], ATHINAS[3], GEOPONIKI[4], PATISION[5], PERISTERI[6], MARPOUSI[7]) of the Ministry of Environment (Directorate of Air and Noise Pollution Control). The geographical distribution of these stations is shown in Figure 1.

The assessment of NO_x concentrations was succeeded by treating NO and NO_2 as a single primary pollutant, because of the very rapid chemical conversion of the emitted NO to NO_2, (Kalabokas *et al.*, 1999). For that purpose, NO is converted to NO_2 and the unit used is $\mu g\ m^{-3}$ "NO_2 equivalent". It was found that annual variation of NO_x is mainly due to NO, because of the NO_2 annual variation is not significant, as the winter values are quite similar to the summer ones. This confirms Kalabokas *et al.* (1999) findings.

For the harmonic analysis of the annual variation of NO_x concentration, using mean monthly values, the following formula, which is the most common for meteorological and climatological research, is applied (Conrad and Pollak, 1950):

$$y = \alpha_0 + \alpha_1 \sin\left(\frac{2\pi t}{12} + \phi_1\right) + \alpha_2 \sin\left(\frac{2(2\pi t)}{12} + \phi_2\right)$$

$$+ \ldots + \alpha_k \sin\left(\frac{k(2\pi t)}{12} + \phi_k\right) + \ldots =$$

$$\alpha_0 + \sum_{k=1}^{n} \alpha_k \sin\left(\frac{2k\pi t}{12} + \phi_k\right)$$

where α_o is the arithmetic mean of the mean monthly values, α_1, α_2, ... , $\alpha_\varkappa$ are the amplitudes and φ_1, φ_2, ... , $\varphi_\varkappa$ are the phase angles of the respective harmonic terms with k=1, 2, 3, ...

The application of the mentioned formula was succeeded for k=2, because the annual variation of the NO_x concentration is well described with two harmonic terms, which explain more than 90% of the total variance. In the process, the time of maximum NO_x concentration is evaluated, for each station, using the formula:

$$t_{\max} = \left(\frac{\pi}{2} - \phi_k\right)\frac{12}{2k\pi}$$

Table 1 presents the results of the Fourier analysis. It is crystal clear that the percentage of the total variance explained by the first harmonic is high enough, so that the variation of the first harmonic is quite similar to the annual variation of the original data. The amplitude of the first harmonic appears to be higher in the center of Athens (Patision, Athinas) than in the suburbs, probably because of the car traffic, which decreases during the summer in the center of Athens while increases in the suburbs. The amplitude of the second harmonic is also larger in the center of Athens than in the suburbs.

Comparing the amplitudes of the first and second harmonic components, each station to Patision station, which is the most polluted station, the following results are obtained (Table 2):

As the first harmonic is concerned, the amplitude in Smirni is 39% of that in Patision, while in Athinas the ratio is 92%. The high ratio for Piraeus (60%) may be explained by the industrial activity and that of the port. Examining the second harmonic, the minimum ratio is observed in Geoponiki (19%), while the maximum appears in Athinas (56%). It is remarkable that the stations near the coast line (Piraeus, Smirni) present a quite low ratio, probably due to the sea breeze, which pushes the pollutants in the interior of the Attica basin.

Table 1. Geographical position of the stations (Latitude, Longitude) and Fourier results, (a_1, a_2: the amplitudes of the first and second harmonic term and t_1, t_2: the time of maximum for the first and second harmonic term, respectively).

	Station	Latitude	Longitude	a_1 μg m^{-3}	t_1 DATE	%	a_2 μg m^{-3}	t_2 DATE	%
1.	N. Smirni	37°55.974	23°42.900	31.1	7 JAN	73.7	16.2	8 JUN	19.9
2.	Piraeus	37°56.607	23°38.857	47.1	2 JAN	88.1	15.3	6 JUL	9.3
3.	Athinas	37°58.681	23°43.620	72.7	3 JAN	90.5	22.2	17 JUN	8.5
4.	Geoponiki	37°59.028	23°42.436	37.9	27 JAN	91.6	7.5	21 JUN	3.6
5.	Patision	37°59.958	23°43.977	79.0	16 JAN	72.9	39.4	26 MAY	18.1
6.	Peristeri	38°00.911	23°41.767	46.3	10 JAN	75.3	21.2	2 JUN	15.8
7.	Marousi	38°01.858	23°47.281	48.8	26 DEC	85.8	15.2	29 MAY	8.3

Table 2. Ratios of amplitudes of air pollution stations in Athens basin.

Amplitude	SMI/PAT	PIR/PAT	ATH/PAT	GEO/PAT	PER/PAT	MAR/PAT
1st harmonic	0.39	0.60	0.92	0.48	0.59	0.62
2st harmonic	0.41	0.39	0.56	0.19	0.54	0.39

Table 3. Theoretical equations for the evaluation of NO_x concentration (μg m^{-3}), as they are described with two harmonic terms (t: the month of the year, t=0 corresponds to January 16 and so on).

	Station	**NO_x Concentration (μg m^{-3})**
1.	N. Smirni	$C_{SM} = 73.7 + 31.1 \sin[(2\pi/12)t + 1.74] + 16.2 \sin[(4\pi/12)t + 2.94]$
2.	Piraeus	$C_{PI} = 167 + 47.1 \sin[(2\pi/12)t + 1.81] + 15.3 \sin[(4\pi/12)t + 1.97]$
3.	Athinas	$C_{AT} = 215.1 + 72.7 \sin[(2\pi/12)t + 1.79] + 22.2 \sin[(4\pi/12)t + 2.64]$
4.	Geoponiki	$C_{GE} = 136.1 + 37.9 \sin[(2\pi/12)t + 1.38] + 7.5 \sin[(4\pi/12)t + 2.48]$
5.	Patision	$C_{PA} = 359.3 + 79.0 \sin[(2\pi/12)t + 1.56] + 39.4 \sin[(4\pi/12)t + 3.39]$
6.	Peristeri	$C_{PE} = 126.7 + 46.3 \sin[(2\pi/12)t + 1.68] + 21.2 \sin[(4\pi/12)t + 3.15]$
7.	Marousi	$C_{MA} = 94.1 + 48.8 \sin[(2\pi/12)t + 1.94] + 15.2 \sin[(4\pi/12)t + 3.29]$

The analytical equations, as they derived by applying Fourier analysis to the mean monthly NO_x data, that evaluate the NO_x concentrations, for each one station, are presented in Table 3. It has been mentioned that using these mathematical models, the computed NO_x concentrations reach more than 90% of the observed mean monthly concentrations.

The annual variation of the NO_x concentrations, as they are theoretically computed, for the first, together with the second harmonic component are shown in Figure 2. It is useful, from that point of view, to determine the annual variation of the first component as the result of the anthropogenic factor (the heavy car traffic).

The maximum of the first harmonic appeared in winter (see also Table 1) is mainly due to the road traffic while the summer minimum is due to the reduced private car traffic during July-August vacations and the intense flow of the "Etesians" winds. Also another possible reason for the summer minimum is the oxidation of both NO and NO_2 under the intense solar activity.

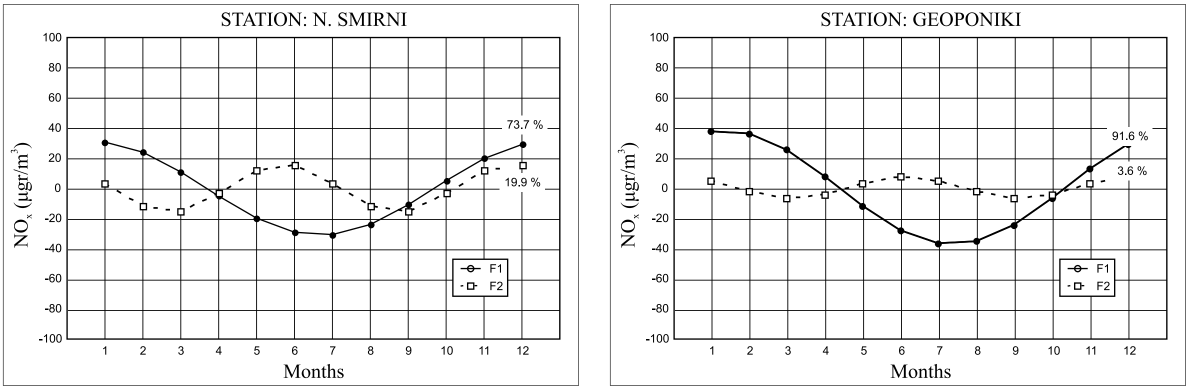
The annual variation of the second harmonic component (Figure 2) reveals the influence of the meteorological factor. The maximum appeared in late spring or early summer is due to sea breeze, which is more often for that period of the year. It is well known that the circulation of sea breeze is appeared during warm days with weak pressure patterns. The sea breeze tends to stratify the atmosphere above the city, with the result of temperature inversion that traps the pollutants near the ground.

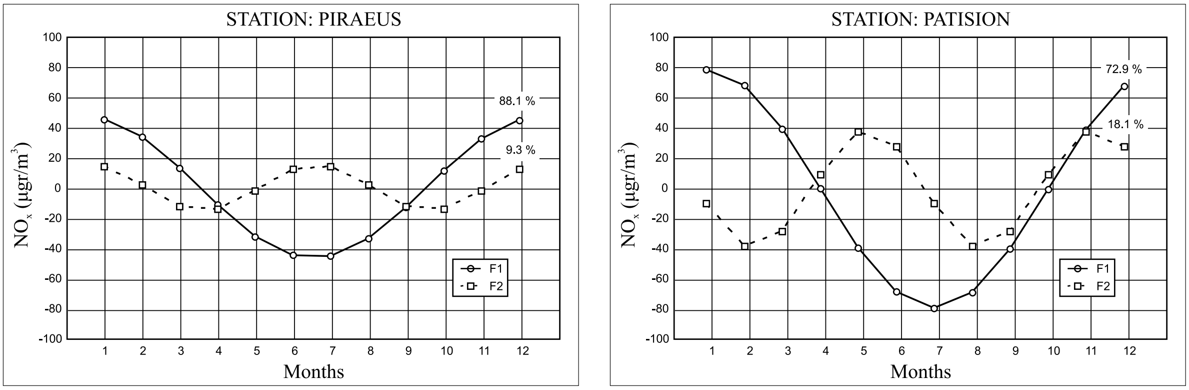
The association of sea breeze with air pollution episodes has been recognized long ago (Lalas *et al.*, 1983; Kallos *et al.*, 1993). Also, the regime of the "Etesians", the northerly high summer winds, is interrupted occasionally by the passage of weak pressure troughs (Repapis *et al.*, 1975), giving way to stronger sea breeze reaching the boundaries of the urban city, in a long distance from the sea.

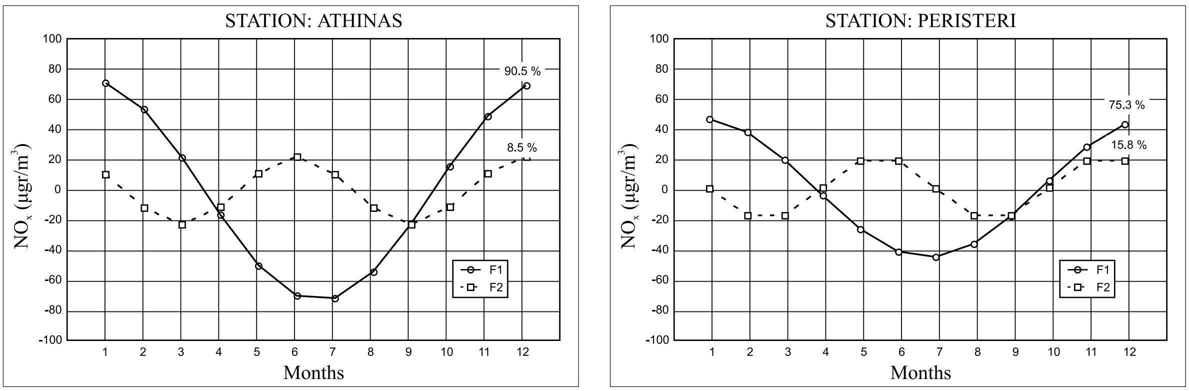
The Figure 3 presents the Box & Whiskers diagrams for the mean monthly NO_x concentrations, where the mean annual value with standard error and extremes limits, for each station are plotted. It is obvious the high levels of the polluted stations of the network [Patision (359.31 μg m^{-3}), Athinas (215.01 μg m^{-3}), Piraeus (166.95 μg m^{-3})].

In order to examine the spatial distribution of the time of maximum NO_x concentrations in Athens basin, first, the dates were estimated by the contribution of the phase angle of the k-harmonic component and in the process, the use of Kriging method (Nastos, 1993) gives the isopleths of the time of maximum in the area under investigation. The results for the first and second harmonic are plotted in Figure 4.

As the time of maximum for the first harmonic is concerned, the pattern of isopleths shows that there is a time shift of about a month later between the peripheral stations and the urban center. The maximum of NO_x happens in the last days of December for Marousi and early in January for Piraeus, Athinas, and N. Smirni and after the middle of January in Patision and Geoponiki. The spatial distribution of the time maximum for the second harmonic indicates a more reasonable pattern.







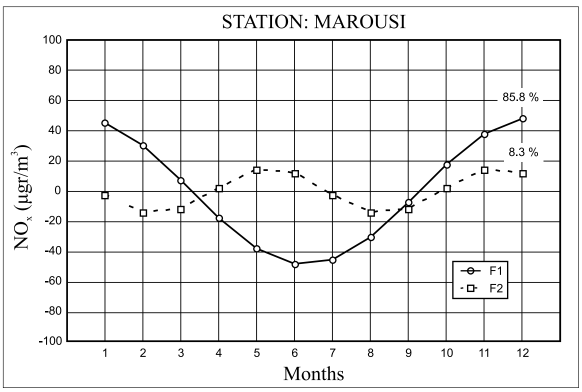


Figure 2.
Annual variation of the NO_x concentration, as it is described by the first harmonic (F_1) and the second harmonic component (F_2), along with the percentages explained of the total variance.

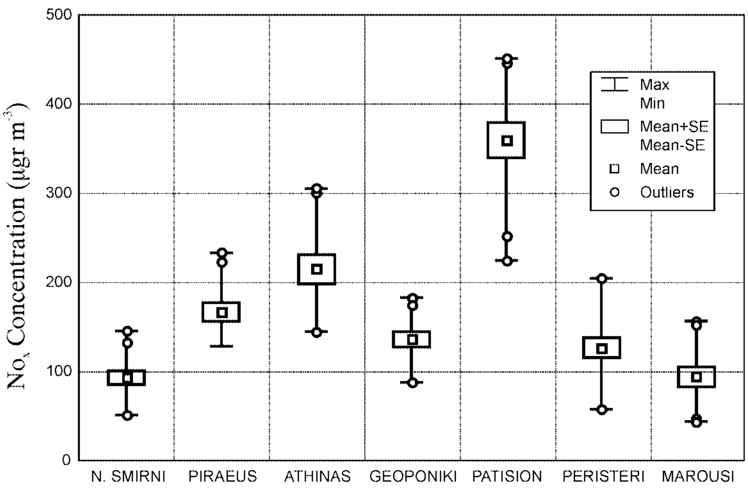


Figure 3. Box & Whiskers diagrams of mean monthly NO_x concentrations for the period 1989-1999.

The maximum appears in Marousi, late in the spring (29 May) and little by little it moves towards the sea (Piraeus, 6 July) following the NE direction. This phenomenon can be explained by the strong development of sea breeze during late spring and early summer. Sea breeze circulation can be appeared during more than 30% of the days in spring and summer months in Athens (Prezerakos, 1986). As the time goes by and the regime of the "Etesians" winds is established during the summer months, the maximum of NO_x is spread towards the sea, due to sea breeze weaking.

CONCLUSIONS

The annual variation of the NO_x concentration for each of the 7 stations of the air pollution automated network is well described with two harmonic terms, which explain more than 90% of the total variance. Probably, the first harmonic component concerns the anthropogenic factor (the heavy car traffic), while the second one the meteorological factor (the development of the sea breeze and the northeastern flow of the "Etesians" winds).

As the time of maximum for the first harmonic is concerned, the pattern of isopleths shows that there is about a month shift between the peripheral stations and the urban center. The spatial distribution of the time maximum for the second harmonic indicates a more reasonable pattern. The maximum appears in Marousi late in the spring (29 May) and little by little it moves towards the sea (Piraeus, 6 July) following the NE direction. This can be explained by the development of sea breeze, which is strong during the days in the late spring and early summer.

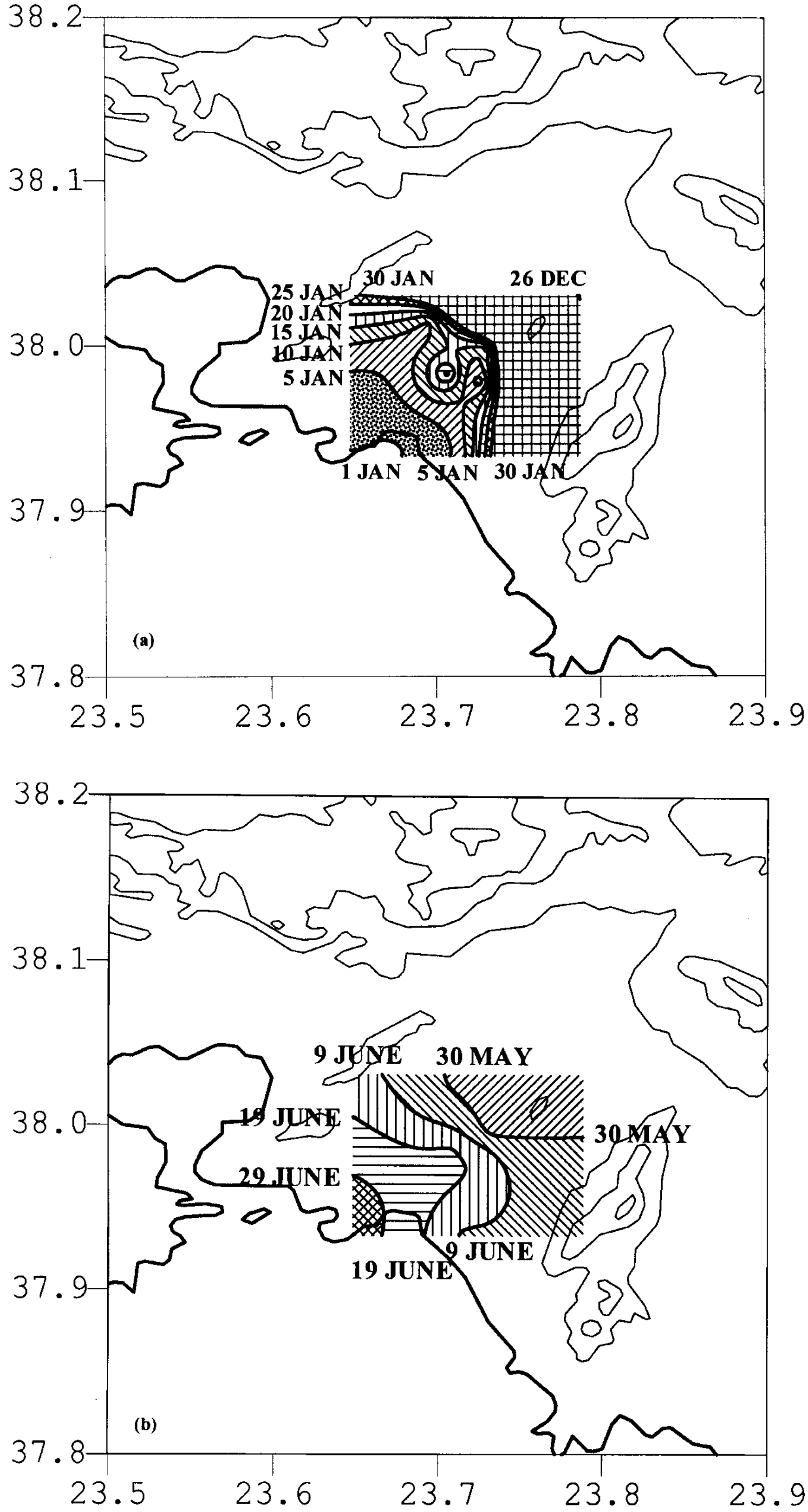


Figure 4. Spatial distribution of the time of maximum of NO_x concentrations for the first harmonic (a) and for the second harmonic (b).

REFERENCES

Conrad, V. and Pollak, L.W. (1950), Methods in Climatology, Harvard University Press, Cambridge, Massachusetts, 118-133.

Kallos, G., Kassomenos, P. and Pielke, R.A. (1993), Synoptic and mesoscale weather conditions during air pollution episodes in Athens, Greece, *Bound. Layer Meteorol*., **62**, 163-184.

Kalabokas, P.D., Viras, L.G., Repapis C.C. and Bartzis J.G. (1999), Analysis of the 11-year record (1987-1997) of the air pollution measurements in Athens, Greece. Part I: Primary Air Pollutants, *Global Nest: the Int. J*., **1**, 157-167.

Lalas, D., Asimakopoulos, D., Deligiorgi, D. and Helmis, C. (1983), Sea-breeze circulation and photochemical pollution in Athens, Greece, *Atmos. Environ*., **17**, 1621-1632.

Mantis, O., Repapis, C., Zerefos, C. and Ziomas, J. (1992), Assessment of the potential for photochemical air pollution in Athens: A comparison of emissions and air pollutants in Athens with those in Los Angeles, *J. Appl. Met*., **31**, 1467-1476.

Min. of the Env. Report, (1998), Attiki-SOS, Atmospheric Pollution in Athens, 1994-1997, Ministry of Environment.

Nastos, P., (1993), The interpolation method Kriging and application in Climatology, In: *3rd Hellenic Geographical Congress*, Athens, 547-555.

Prezerakos, N.G. (1986), Characteristics of the Sea Breeze in Attica, Greece, *Bound. Layer Meteorol*., **36**, 245-266.

Repapis, C.C., Zerefos, C.S. and Tritakis, B. (1975), On the Etesians over the Aegean. In: *Proc. Acad. Athens*, **52**, 572-606.

Ziomas, I., Suppan, P., Rappengluck, B., Balis, D., Tzoumaka, P., Melas, D., Papayiannis, A., Fabian, P. and Zerefos, C. (1995), A contribution to the study of photochemical smog in the Greater Athens area, *Beitr. Phys. Atmosph.*, **68**, 191-203.