AN ANALYSIS OF THE SO₂ CONCENTRATION LEVELS IN ATHENS, GREECE

D. P. LALAS*[†], V. R. VEIRS[‡], G. KARRAS* and G. KALLOS*

*Department of Meteorology, University of Athens, Greece; †Also with the Department of Mechanical Engineering, Wayne State University, Detroit, MI, U.S.A.; ‡Department of Physics, Colorado College. Colorado Springs, CO, U.S.A.

(First received 27 January 1981 and in final form 8 April 1981)

Abstract—In this paper, an analysis of the meteorological parameters that affect SO₂ pollution in Athens. a problem of both local and international concern, is presented. The influence of these meteorological parameters on the SO₂ concentrations has been investigated by a statistical analysis of the daily average SO₂ values measured at six locations in the Athens basin for the six years from 1974 to 1979. Wind speed, minimum temperature and amount of rain has been found to control SO₂ concentrations during the cold season while wind speed, wind direction and relative humidity are central in the warm season. Based on this, multiple regression models, both linear and non-linear, for the prediction of the next day's SO₂ concentration have been derived that explain more than 50% of the data variance. Further improvements on the modelling are contingent on the availability of boundary layer structure data and on details of the local wind field. The onset and end of such episodes have been identified. Finally, discriminant analysis classification functions, utilizing forecast meteorological variables have been obtained which are capable of predicting accurately the occurrence of high pollution concentrations.

1. INTRODUCTION

In the last twenty years population shifts and increased overall industrialization have resulted in the tripling of the population and activity in the Athens, Greece area. As a direct consequence pollution has reached alarming levels and has become a hazard to both human beings and valuable objects such as the ancient monuments, with the most notable and noticeable among them the Acropolis (Vermeule, 1977; Yocom, 1979). Visual proof of the existing high levels of pollution is the photochemical cloud that has become as permanent a feature in Athens as it is in Los Angeles. Its intensity has, on occasion (for example, during the period of 24-28 September 1979), been so strong that it has caused near hysteria of the population, increased admissions to the hospitals, etc. Hourly ozone levels in downtown Athens exceeded 80 ppb every day and 120 ppb eleven times during the three summer months of 1980.

The damage that air pollution causes to ancient monuments is well known and has become a subject of international concern (Proceedings of the 2nd Int. Symposium on the Deterioration of Building Stone, 1976; Yocom and Upham, 1978). Most of the deterioration of marble, of which the majority of the Classical and Roman buildings in Greece and Italy are made, is the result of calcification of the surface layer by SO_2 and especially SO_3 which leads to surface crumbling. The catastrophic action of SO_2 on marble, in addition to its adverse effects on health, and the existence of a substantial time series of data have led us to the present study of SO_2 pollution in Athens, the results of which we hope will provide insight for the choice of tactics for halting environmental deterioration and for wisely planning urban renewal.

Thus, after a description in section 2 of the local geography and climatology, we describe in section 3 the available data for air pollution and meteorological parameters. Then, in section 4, we present concentration levels and comment on their geographic variation. In section 5 we discuss the effect of meteorological parameters on air pollution, and working from this discussion, we examine in section 6 the conditions for high concentration episodes and summarize our conclusions in section 7.

2. GEOGRAPHY, CLIMATE AND POLLUTION SOURCES OF THE ATHENS BASIN

As can be seen in Fig. 1, Athens with an estimated population of 3.5 million in 1980, is located in a basin of approx. 450 km² surface area with fairly high mountains on three sides (Aegaleo to the west, Parnitha and Penteli to the north, Hymettos to the east) and the sea on the fourth. The basin is oblong with a SW-NE major axis about 30 km long and is bisected by a series of small hills. Most industrial activity is located in the southwest, near the Pireas harbor, and consists of major textile and food-processing plants but also includes cement, chemical, fertilizer, paint, and paper factories as well as a large number of small plants producing a variety of other products. In addition, refineries, shipyards, and a steel mill are located on Eleusis bay west of Mount Aegaleo. The ships in the main harbor of Pireas and the airplanes of Ellinikon airport also contribute significantly to pollution. The



Fig. 1. Map of the Athens basin. Residential areas are indicated by stippling and industrial areas by cross-hatching. Also indicated are the peaks of major mountains and their elevations in meters as well as the 100 m (dashed line) and 500 m (dot-dashed line) contours. The locations of the six National Observatory of Athens stations are marked by their respective numbers (151 to 156), and the main Athens power plant at Keratsini is marked by a capital

К.

largest point source in the Athens region is the oilburning electrical power station at Keratsini with an average discharge rate of 1.5 kg s^{-1} of SO₂ out of a 155 m stack.

The climate of Athens is mediterranean with hot, dry summers and wet, mild winters. The average daily winter (Dec., Jan., Feb.) temperature is 9.9° C, and the daily minimum temperature drops below freezing only twice a year. In the summer months (June, July, Aug.) the average daily temperature is 25.8° C although the average daily maximum temperature is more than 31° C. Most of the rainfall (418 mm annually) occurs in early October and the winter months, when travelling winter weather disturbances pass north of the city causing cold and warm fronts to sweep alternately across Athens. In the summer only infrequent, severe local thunderstorms of very short duration produce noticeable precipitation. The insolation is strong with average daily values (average global solar radiation on a horizontal surface) of the order of 22 MJ m^{-2} in the summer and 8 MJ m^{-2} in the winter. This usually accounts for a fairly deep mixed layer (Asimakopoulos *et al.*, 1980) but also provides the driving force for seabreeze circulation. The sea-breeze cell develops along the main SW-NE axis of the basin, which is also perpendicular to the shoreline. An additional cell, which is usually stronger, is established in the plain E of Mount Hymettus (see Fig. 1) and results in some inflow through the pass between the Hymettus and Penteli mountains.

The winds blow mostly along the N-NE/S-SW axis (Fig. 2) with the prevailing wind direction being NNE in the late summer, fall and winter and SSW in the spring and early summer. This axis coincides with the major geographic axis of the basin but is not directly caused by channeling. The predominance of the north sector winds is due to the existence of regional Eastern Mediterranean weather patterns that result in local



Fig. 2. (a) Average (1925–1975) wind roses for Athens (National Observatory of Athens site) at different months of the year with the frequency of occurrence of calms, light (less than 6 knots), moderate (between 7 and 21 knots), strong (between 22 and 33 knots) and exceptionally strong (larger than 34 knots) winds also indicated. (b) Wind roses for all the days in the 1974–1979 period and for days with daily SO₂ concentration larger than 250 µg m⁻³ (episode days).

strong north winds, i.e. the Bora in the winter and the Etesians in the summer (*Weather in the Mediterranean*, 1965; Metaxas, 1977; Karapiperis and Catsoulis, 1977). The second predominant wind direction, i.e. SSW, is usually associated with lower speeds (typically less than 2 m s^{-1}) and is caused by anticyclonic conditions or comprises the warm sector flow of travelling disturbances. In the spring and early summer the southerly flow is probably due to sea-breeze circulation.

Most of the SO_2 released in the air comes from burning fossil fuel. For example, the latest published data, for 1973 (Table 1), indicate that only 10% of the SO₂ released is attributable to non-combustion sources. As much as 80% of the SO₂ comes from heavy residual oil, which typically has a sulfur content of 3.5-4.0%. Unfortunately, published up-to-date source inventories are not available, but it is reasonable to assume that the allocation to the various sectors of activity remains the same today except perhaps for a small decrease in the percentage for space heating with heavy residual oil, the use of which was banned in January 1978. It should be pointed out, though, that this change is responsible for less than 10% of the total

Table 1. Sources of SO, pollution for Athens in 1973* (in metric tonnes per year)

| | Tonnes y ⁻¹ |
|---------------------------------------|-------------------------------|
| Space heating (distillate oil) | 6350 (4 °) |
| Space heating (heavy residual oil) | 7700 (5 °) |
| Industries-energy production (dis- | . 0 |
| tillate oil) | 2130 (1°.) |
| Industries-energy production | , 0. |
| (heavy residual oil) | 57280 (37°) |
| Electricity production (heavy re- | |
| sidual oil) | 54000 (35°) |
| Cars and railroads (distillate oil) | 6650 (4°) |
| Railroads (heavy residual oil) | 5600 (3 °്) |
| Industrial activity other than direct | |
| burning | 16000 (10 °) |
| - | 155710 tonnes y ⁻¹ |
| Heavy residual oil has 3.5 to 4.0 ° | |
| sulfur | |
| Distillate oil has 1 % sulfur | |

* From Interim Technical Report. Environmental Monitoring and Protection Bureau, Greek Ministry of Social Services.

production of SO₂, even if its seasonal pattern of use is taken into account and the numerous exceptions to the prohibition order are ignored. However, this reduction may be more significant locally because it affects area sources, the effluents of which do not advect far. The increase of the number of vehicles is noticeable, but its added contribution is partially offset by the alternateweekend driving regulation put in effect in 1979. (Under this regulation cars with license plates ending in odd numbers are allowed to operate one weekend, with even-numbered cars the next weekend; so on any weekend only half the cars are in operation.)

3. METEOROLOGICAL AND AIR POLLUTION DATA

The data that have been used in this study have been obtained by the network of stations operated by the Meteorological Institute of the National Observatory of Athens (henceforth MINOA). These data are published annually in the Air Pollution Bulletin and the Climatological Bulletin of MINOA. MINOA is located in the center of the Athens basin, within 500 m of the Acropolis, on a small hill at an altitude of 107 m above MSL. Continuous measurements of all meteorological parameters have been carried out at this site since 1870. Starting in 1969, MINOA has operated a network for pollution monitoring, which since 1974 comprises six stations. These stations measure daily values (24 h) of SO, by the hydrogen peroxide method and smoke by reflectometry of filters utilizing British National Survey sampler bubblers. (For a brief description of some of the shortcomings and interferences of these instruments and methods see Barnes, 1976).

The Bureau for Environmental Protection of the Ministry of Social Services also monitors SO_2 in the Athens area via the West–Geake method, but because

of changing policy requirements, the Bureau does not possess uninterrupted long records in as many sites as MINOA nor does the Bureau monitor all the meteorological parameters at any of its stations. At locations where MINOA and Bureau stations are near each other, SO_2 values correlate well, despite the difference in the measurement techniques.

Of the six MINOA stations, one (151) is located at the Institute, near the Acropolis, one (152) is in the center of the business section of Athens, two (155 and 156) are in urban residential areas, one (153) is in the industrial zone and the last (154) is on the shoreline near the Pireas harbor and business district. Taken together, they provide a representative coverage of the Athens basin.

4. CONCENTRATION LEVELS

In Fig. 3, the average monthly values of the SO₂ concentrations of four stations for the period from 1974 to 1979 are presented. The mean monthly values of wind speed, minimum daily temperature and duration of rain, for the same period, are shown in Fig. 4. Perusal of the SO₂ time series shows maxima in December-January and minima in September-October. Station 153, which is located in the middle of the industrial area, exhibits much smaller winter-summer fluctuation and a second maximum in early summer. The minimum in the early fall is the result of the relatively high duration of rain combined with the deep mixed layer which results from the high surface temperatures.

A general trend toward smaller winter maxima seems to exist, but investigation of the complete time series for stations 151 and 153, which start as far back as 1970, reveals that the large concentrations of the winters of 1974-1975 and 1975-1976 are exceptional and can be explained for the most part by the climatological conditions as described in a later section. The measured values at all the stations especially 151, 152, 155 and 156, seem to be well correlated with each other, as can be seen in Table 2, where mean values and correlations of the average daily values of all stations with each other are shown. The least correlated station is 153. This can be attributed primarily to its location in the midst of the industrial region, where it is under the influence of large nearby point sources. Thus its behavior is different from that of the other stations, especially during the summer months (as is evident in Fig. 3) when industrial activity remains high, while traffic diminishes and space heating is not present. The slightly lower correlation coefficients for 154 are primarily attributable to its location on the shoreline, which makes the concentration levels susceptible to local boundary layer phenomena, such as differences in the mixed layer depth resulting from the sudden change of surface roughness (Taylor, 1969; Jensen and Peterson, 1978). High correlations (wherever it is feasible to calculate



Fig. 3. Monthly average values of daily SO₂ concentration in $\mu g/m^3$ at three stations (151, solid line; 153, dashed line; and 155, dot-dashed line) in Athens. Station 155 started operation in May 1974.



Fig. 4. Monthly values at the National Observatory of Athens meteorological station (151) of average wind speed in m s⁻¹ (solid line), total duration of rain in hours (dashed line) and minimum temperature in ²C (dot-dashed line) for the period 1974-1979.

them) are also found between the daily SO_2 values measured by the Ministry of Social Services and the MINOA stations. Separation of the data in warm (15 April to 15 October) and cold (15 October and 15 April) periods and subsequent analysis show lower correlations for the warm period, when SO_2 concentrations are lower and the large area sources do not contribute; thus the uneven distribution of point sources and traffic patterns becomes evident.

In Fig. 5 the correlations between 151 and all the others lagged in time are shown. The auto- and cross-correlations remain substantial for a one-day lag and also hint at the existence of a seven-day cycle. The noticeable one-day lagged correlation, due to residual rather than background pollution, will be utilized in the next section to develop predictive models.

5. RELATION OF SO₂ CONCENTRATIONS TO METEOROLOGICAL PARAMETERS

In order to understand and predict air pollution concentration levels and patterns, deterministic numerical models which parametrize diffusion processes in various degrees of sophistication have been developed by many investigators. A necessary (but not sufficient) ingredient for any numerical model is a good source inventory. Since such an inventory is not available for the Athens basin, a statistical approach would appear to be more fruitful. Thus, the influence of various meteorological parameters has been investigated, and based on the results, some simple but effective statistical models have been developed.

The meteorological parameters that affect air pol-

| Station No. | 151 | | 152 | | 153 | | 154 | | 155 | | 156 |
|----------------|----------------|--------|----------------------|--------|----------------------|--------|----------------------|--------|----------------------|--------|----------------------|
| 151 | 91.1 (72.9) | W C | 0.84 0.86 0.57 | | 0.57 0.60 0.61 | | 0.70 0.42 0.71 | | 0.82 0.44 0.87 | | 0.78 0.67 0.80 |
| 152 | <u>2094</u> | | 110.1 (99.0) | W C | 0.52 0.54 0.60 | | 0.69 0.39 0.70 | | 0.86 0.89 0.61 | | 0.83 0.66 0.83 |
| 153 | <u>2141</u> | | <u>2076</u> | | 106.7 (61.6) | W C | 0.51 0.40 0.60 | | 0.52 0.53 0.63 | | 0.62 0.62 0.71 |
| 154 | <u>2059</u> | | <u>1994</u> | | <u>2057</u> | | 97.0 (60.0) | W C | 0.72 0.38 0.73 | | 0.71 0.43 0.71 |
| 155 | <u>2024</u> | | <u>1958</u> | | <u>2021</u> | | <u>2034</u> | | 91.8 (81.1) | W C | 0.87 0.59 0.89 |
| 156 | <u>1800</u> | | <u>1731</u> | | <u>1802</u> | | <u>1806</u> | | <u>1784</u> | | 100 (68.9) |

Table 2. Correlations of the daily SO₂ values measured at the various MINOA stations for the period 1 January 1974 to 31 December 1979 (except for 155 which started operating on 1 April 1974; and 156, which started on 1 January 1975)

Three correlations are given for each pair of stations, the overall one first, then one for the warm period, 15 April to 15 October of all years, and a third one for the cold period, 15 October to 15 April, when space heating is in operation. The values on the diagonal are the mean SO_2 concentrations in μ gm⁻³ and those in parentheses are the standard deviations for each station. Below the diagonal, underlined, are the numbers of pairs utilized for the various correlations.



Fig. 5. (a) Lagged cross-correlations of SO_2 daily concentrations between station 151 and all the others (152 to 156). The abscissa is the lag in days of the various stations relative to 151. (b) Lagged auto-correlation of station 151.

lution concentrations include wind speed, wind direction, temperature, precipitation, humidity, as well as inversion height and stability. We chose to examine the first five parameters, because inversion height measurements were not available for the whole period from 1974 to 1979, and stability is known (Lalas *et al.*, 1979) to vary substantially from point to point in the Athens basin, so that no average would be meaningful

in such inhomogeneous topography. In addition, it was decided that the daily minimum temperature would be the most appropriate temperature, since it usually occurs in the early morning hours when many building superintendents decide whether or not to operate the heating system for the day; hence, the minimum temperature can be expected to relate to the daily SO₂ emission rate from area sources. The meteorological data are from the central MINOA meteorological station adjacent to station 151. The interrelations of the meteorological variables have been briefly discussed in section 2 and are also presented in Table 3. The strong correlation between wind direction and minimum temperature and between wind speed and rain duration in the cold period, but not in the warm one, should be noticed. In Table 4(a), straightforward linear correlations are shown between all MINOA stations and the various meteorological parameters. In view of the high autocorrelation coefficients of Fig. 5(b) for one-day lags for station 151 and numerous indications in the literature (Tiao et al., 1975; Finzi et al., 1979), the correlation with the previous day's concentration is also included. A first look at Table 4(a) brings out the fact that indeed the previous day's concentration is important in determining the air pollution concentration. Predictably, this is less so for station 153, where factories, i.e. point sources, predominate and the residual is most likely low, since the pollutants are released from stacks and are transported farther away. The same is true for the effect of minimum temperature, which is negligible for 153 but important for the others. The wind speed, on the other hand, is equally important at all stations. as is the wind's persistence. Although both the NW and NE wind directions are important, the NE is more significant because of the predominance of N-NE winds. This is most evident for station 153 again, since the sources around it are stacks, and so the transport of their effluents is directly affected by wind direction. The concentrations at all stations are influenced, to slightly different degrees, by washout, which is proportional to both the amount and duration of rain. Finally, relative humidity, in view of its significance levels, does not seem to play a consistent role.

Since the sources change between the warm and cold periods, the relation between the main meteorological variables and the concentrations has been examined separately for the cold and warm periods and is shown in Table 4(b). Here it becomes evident that the minimum temperature is a much more important

| Table 3. | Simple linear | correlations | between | various | meteorological | parameters | for | 1974-1979 in Athen | s |
|----------|---------------|--------------|---------|---------|----------------|------------|-----|--------------------|---|
| | | | | | | | | | |

| | Rain amount | Rain duration | Minimum temperature | Wind speed | NE direction | NW direction | Wind persistence | Relative humidity | y |
|---------------|----------------|------------------|------------------------|---------------|-----------------|-----------------|------------------|----------------------|---|
| Rain amount | | 0.65 | - 0.01 ⁺ | 0.13 | 0.08* | 0.03+ | 0.01+ | 0.34 | С |
| Rain duration | 0.72 | | -0.20 | 0.32 | 0.18 | 0.09 | 0.09 | 0.42 | 0 |
| Minimum | | | | | | | | | L |
| temperature | -0.15 | -0.25 | | -0.17 | -0.35 | -0.30 | -0.02+ | 0.07* | D |
| Wind speed | -0.07* | 0.06* | 0.05† | | 0.29 | 0.08* | 0.49 | -0.05* | |
| NE direction | 0.01† | 0.02+ | 0.14 | 0.49 | | 0.33 | 0.19 | -0.04† | Р |
| NW direction | -0.08* | -0.02+ | 0.03+ | 0.17 | 0.31 | | $-0.01 \pm$ | -0.27 | E |
| Wind | | | | | | | | | R |
| persistence | -0.13 | 0.14 | 0.06* | 0.55 | 0.13 | -0.08* | | - 0.05* | I |
| Relative | | | | | | | | | 0 |
| humidity | 0.28 | 0.37 | - 0.52 | - 0.30 | - 0.36 | 0.16 | -0.14 | | D |
| | | | | WAR | M PERIOI | C | | | |

The lower part of the table (below the diagonal) is for the warm period (15 April to 15 October, 1103 days) and the upper part for the cold period (15 October to 15 April, 1086 days). The *correlations have significance levels larger than 0.001 and the *correlations have significance levels larger than 0.05. The NE variable is defined as $[1 + \sin(\phi + 45^{\circ})]$ with $\phi = 0^{\circ}$ for north so that it is largest for NE winds and smallest for SW winds while the NW variable, defined as $[1 + \cos(\phi + 45^{\circ})]$, is largest for NW and smallest for SE winds.

Table 4(a). Correlation coefficients between the SO₂ daily concentrations of various stations and the meteorological variables recorded at MINOA (station 151) for the years 1974 to 1979

| Station No. | 151 | 152 | 153 | 154 | 155 | 156 |
|-----------------------------|---------|-------|---------|---------|---------|---------|
| Min. temp. | -0.25 | -0.38 | - 0.04 | - 0.40 | - 0.46 | - 0.35 |
| Rain duration | -0.16 | -0.12 | -0.26 | -0.11 | -0.07 | -0.13 |
| Rain amount | -0.13 | -0.12 | -0.20 | -0.12 | -0.09 | -0.13 |
| Wind speed | -0.32 | -0.26 | -0.28 | -0.21 | -0.25 | -0.25 |
| NE direction* | -0.12 | -0.11 | -0.32 | -0.04 | -0.14 | -0.21 |
| | | | | (0.029) | | |
| NW direction* | - 0.07 | -0.07 | -0.03 | 0.06 | -0.06 | -0.07 |
| | | | (0.086) | (0.004) | (0.002) | |
| Wind persis. | -0.17 | -0.10 | -0.12 | -0.09 | -0.10 | -0.11 |
| Rel. humidity | -0.01 | 0.08 | -0.19 | 0.00 | 0.16 | 0.01 |
| - | (0.287) | | | (0.465) | | (0.288) |
| Previous day's SO_2 conc. | 0.67 | 0.68 | 0.43 | 0.51 | 0.64 | 0.62 |
| · - | | | | | | |

* For the definition of NE and NW direction variables see caption of Table 3.

The numbers in parentheses represent the level of significance of the correlation if larger than 0.001.

| Station No. | | 151 | 152 | 153 | 154 | 155 | 156 |
|-------------|--------|------------------|------------------|------------------|------------------|------------------|----------------|
| Min. temp. | w c | -0.16 -0.26 | -0.00 -0.26 | - 0.08 - 0.14 | -0.12 -0.33 | -0.15 -0.30 | -0.16 -0.31 |
| Rain dur. | w C | - 0.15 - 0.22 | -0.09 -0.23 | - 0.15 - 0.30 | - 0.08 - 0.23 | - 0.03 - 0.20 | -0.15 -0.22 |
| Rain amt. | W C | -0.10 -0.17 | - 0.06 - 0.19 | -0.11 -0.24 | -0.08 - 0.20 | -0.05 -0.17 | -0.14 -0.19 |
| Wind speed | W C | -0.30 -0.37 | -0.34 - 0.32 | -0.25 -0.29 | - 0.17 - 0.29 | -0.32 - 0.33 | -0.28 -0.31 |
| NE dir. | W C | - 0.38 - 0.06 | 0.46 0.06 | -0.41 - 0.29 | -0.20 -0.02 | - 0.50 - 0.11 | -0.45 -0.20 |
| NW dir. | W C | - 0.29 - 0.06 | - 0.35 - 0.06 | - 0.25 - 0.09 | 0.10 - 0.09 | - 0.36 - 0.05 | 0.39 0.08 |

Table 4(b). Correlation coefficients between the SO2 daily concentrations of various stations and themeteorological variables recorded at MINOA (station 151) for the warm (15 April to 15 October) andcold (15 October to 15 April) periods respectively

The NE and NW wind direction variables are defined as in Table 3.

factor in the winter than in the summer, when the correlations are equal to half the winter values for all stations. Its influence on the sources' strength and on the mixed depth seems strong enough to cause the relatively high (negative) correlation, in the winter despite its coincidence with high speed north winds. The same is true for washout, which is almost nonexistent in the warm period with possible exceptions during the first part of October (see Fig. 4). The wind speed remains equally important in the summer and winter, as opposed to the wind direction, which is much more important in the warm period than in the cold period. This is so because in the warm period, if the wind blows consistently, it will be from the north and will completely ventilate the basin (see Fig. 2(a) and Table 3); otherwise a sea- and land-breeze circulation will be set in motion transporting pollution back and forth rather than dispersing it. Transport from industrial areas to the Athens center or from the center to the outskirts is not clearly discernible because of the collocation of the urban center and the industrial region on the major NE-SW axis of topography and predominant wind direction (see Fig. 1). Increased pollution concentration in the center due presumably to transport from the industrial region would require a southern sector wind, which is usually light and thus itself a sufficient reason for small diffusion and increased pollution.

In the light of the previous discussion, an attempt has been made to utilize the effects of all meteorological parameters in predicting SO_2 pollution. Thus, multiple linear and non-linear regression analyses have been carried out for station 151, which we consider typical of the whole basin and which is located where the meteorological variables are measured. The warm (15 April to 15 October) and cold (15 October to 15 April) periods of each year have been treated separately, and the results are shown in Tables 5(a) and 5(b). These results seem to be in agreement with the tendencies already noted in Tables 4(a) and 4(b): namely, that in the warm period the previous day's concentration, the wind speed and the wind direction are the dominant factors that determine SO_2 air pollution levels, and that in the cold period the factors are the minimum temperature, the previous day's concentration, and the wind speed but not the wind direction. The overall correlation coefficients are of the order found in similar studies (Peterson, 1972; Benarie *et al.*, 1974) and are large enough to be competitive with those obtained by sophisticated. numerical, diffusion-equation-based models, such as Shir and Shieh's (1974).

In an effort to model better the variation of pollution due to meteorology, a non-linear multiple parameter model has also been considered, which utilizes the following equation to predict daily SO_2 concentrations:

$$SO_{2}|_{\text{predicted}} = C_{1}[1 - C_{2}Y_{2}/24][1 + C_{3} \cos Y_{3}]$$

$$[1 - C_{4}f_{4}]/Y_{5}^{c_{5}} + C_{6}f_{6} \qquad (1)$$

where C_1 , C_2 , C_3 , C_4 , C_5 and C_6 are coefficients to be determined by least square best fit and

 Y_2 = duration of rain in hours, Y_3 = direction in radians from SSW, $Y_4 = 10^{\circ}$ C minus the minimum temperature in ${}^{\circ}$ C, Y_5 = wind speed in m s ${}^{-1}$, Y_6 = previous day's SO₂ concentration;

with f_4 and f_6 defined by

 $f_4 = 1 + f_{sh}[1 + max(0, 0.02 Y_4)], f_{sh} = 1.0$ January, February, March, November and December, = 0.5 April and October, = 0.0 May to September, $f_6 = Y_6$ if $Y_5 < 1.5 \text{ m s}^{-1}$, = 0 otherwise.

In this fashion, the effect of wind speed is taken to be in accordance with Gaussian plume formulae, and the previous day's concentration contributes only if the wind speed is low so that no ventilation has occurred. Finally, since no space heating is present in the summer months, and only intermittent contribution is to be expected during the transitional months, a three-step function f_{sh} is utilized, which again comes into effect only if T_{min} is smaller than 10.0° C. A number of similar

| | Overall | | | | | | | | | | |
|------|----------------------------------|-----------------------|------------|----------------|-------------------------|----------------------------|------------------|--------------|---|------------|-----------------------------------|
| | correlation | | | Rain | Rain | Wind | NEt | ₩4 | Wind | Relative | |
| | coefficient r | SO ₂ *-1 | н С) | amount (mm) | duration (h) | speed (m s ⁻¹) | direction | direction | persistance | humidity | Constant (µg m ⁻³) |
| 1074 | 770 | | | | | .0.2 | | | a management of the second of | | |
| 19/4 | 0.00 | (1)67'n | 1 | | I | - 6.5(2) | - 6.0(3) | - | | - 5.4(4) | 77 |
| 1975 | 0.70 | 0.29(2) | I | I | No. of Concession, Name | -6.7(3) | -10.7(1) | ł | 0.14(5) | -0.72(4) | 107 |
| 1976 | 0.67 | 0.29(1) | (| NAME OF T | | - 7.5(3) | -7.5(4) | l | ; | -0.72(2) | 94 |
| 1977 | 0.78 | 0.34(2) | 1.7(3) | WARMAN. | - | | - 14(1) | | | - ().68(4) | 11 |
| 1978 | 0.80 | 0.56(1) | | LIFFEREN - | | | -13(2) | - | - 4.3(4) | -1.0(3) | 154 |
| 1979 | 0.80 | 0.47(1) | ł | VARIANSA | I | - 7.4(3) | -8.1(4) | ***** | | -1.0(2) | 103 |
| | | | | | | | | | | | |
| | cvious days S r the definitio | U ₂ concen | Iration II | 1 µgm '. | | af Tatla 3 | - | | | | |
| IIV | of the indepen | ndent varia | bles cons | idered are | hered in the | a heading T | ha first tarm an | and into the | ning actioners | | ومحمد ما مطر |

Table 5(a). Stepwise linear multiple regression analysis of the SO₂ daily concentrations at Station 151 and available meteorological variables for

amount of variance in the dependent variable. Successive terms explain successively smaller amounts of the variance. Only the significant linear regression coefficients (partial F larger than 2.0) are given and the order of entry into the regression equation is given in parentheses.

| | | | | | The second se | | The second devices and the second s | Constant and | State of the second state | Contraction of the second | and the second se |
|--------|--|--------------------|--------------------------|------------------------|---|---------------------------------------|---|--|---|--|---|
| | Overall correlation coefficient r | $SO_2 _{k=1}^{*}$ | T _{mín} (°C) | Rain amount (mm) | Rain duration (h) | Wind speed (m s ⁻¹) | NE† direction | NW† direction | Wind persistance | Relative humidity | Constant (μg m ^{- J}) |
| 1974-5 | 0.76 | 0.36(2) | - 17(1) | siy tarabat | - | (0) 74 (0) | | | | | 735 |
| 9-5-61 | 0.70 | 0.30(1)) | - 8 1 (2) | ļ | 1 2451 | | | | 1111 | | |
| | | (1)((-)) | (7)1.0 | | (c)cc - | (c) 71 - | | No. of Concession, Name | -0.3(4) | ļ | 784 |
| 19/0-7 | 0.72 | 0.42(1) | - 4.9(2) | į | | - 11 (3) | - | ł | - 4.9(4) | | 236 |
| 19778 | 0.77 | 0.21(3) | -4.2(1) | | - 2.2(4) | -4.5(2) | - 6.6(5) | | | -0.58(6) | 169 |
| 1978-9 | 0.78 | 0.33(2) | -4.4(1) | -2.3(5) | | -8.0 (3) | -12 (4) | | - | (a) an | 149 |

Table 5(b). Stepwise linear multiple regression analysis of the SO₂ daily concentrations at Station 151 and available meteorological variables for

† For the definition of NE and NW variables see caption of Table 3.

The independent variables considered are listed in the heading. Only the significant regression coefficients (partial F larger than 2.0) are given, and the order of entry into the regression equation is given in parentheses. formulations were tried in order to find the sensitivity of the model to the coefficients of f_{sh} or the cut-off windspeed for f_6 , etc., but no substantial difference was found. The results of the non-linear regression analysis are shown in Table 6 for both the warm and cold periods. No improvement over the linear multiple regression model is evident. On the contrary, for the cold period, the uncertainty in coefficient C_1 , which multiplies almost all the others (see Equation 1) casts doubt on the overall usefulness of the non-linear model.

An analysis of the residuals of both the linear and non-linear regression models reveals that, as can also be seen in Fig. 6(a), the variance is mostly due to the high concentrations. The models, both linear and nonlinear, are able to predict satisfactorily the phase of the pollution level changes but not the magnitude. Thus, they underpredict the amount of the sudden increase of the concentration levels on the first day of an episode, and they overpredict it on the last day. The presence of the previous day's concentration as an independent variable, especially in the non-linear model where it is conditional on the wind speed, seems to improve only marginally the prediction of the concentrations in the first and the last day of an episode. The information, which would indeed improve the prediction, is the knowledge of the mixed layer depth (Haagenson, 1979) or the strength of the

 Table 6. Coefficients for non-linear multiple regression model utilizing Equation (1). The coefficients marked by an asterisk have a partial F-ratio below 2.0

| | C ₁ | C 2 | С, | C ₄ | C, | C ₆ | Overall correlation coefficient |
|---------|----------------|--------|---------|----------------|------------|----------------|---------------------------------|
| | | | | Co | old period | | |
| 197475 | -17.3* | 1.15 | -0.01* | -6.9* | 0.20 | 0.58 | 0.80 |
| 1975-76 | -12.6* | 0.90 | 0.01* | -6.2* | 0.11 | 0.74 | 0.71 |
| 1976-77 | 29.1 | 2.07 | - 0.05* | 1.0* | 0.09 | 0.67 | 0.67 |
| 1977-78 | 45.6 | 1.08 | 0.05 | 0.25 | 0.17 | 0.24 | 0.65 |
| 1978-79 | 25.2 | 0.86 | 0.07 | 1.2 | 0.31 | 0.22 | 0.76 |
| | | | | Wa | rm period | | |
| 1974 | 74.8 | 1.71 | 0.03* | 0.47 | 0.18 | 0.13 | 0.56 |
| 1975 | 88.1 | 1.18 | 0.11 | 0.60* | 0.16 | 0.04 | 0.70 |
| 1976 | 76.3 | -0.14* | 0.10 | -0.38 | 0.11 | 0.14 | 0.65 |
| 1977 | 97.6 | 2.14 | 0.13 | -0.49 | 0.08 | 0.12 | 0.63 |
| 1978 | 86.6 | 2.17 | 0.24 | -0.85 | -0.18 | 0.12* | 0.52 |
| 1979 | 88.1 | 0.86 | 0.06 | -0.53 | -0.03* | 0.19 | 0.61 |





Fig. 6. (a) Observed vs predicted, by a linear multiple regression model, daily SO₂ concentrations for Athens in the cold period (15 October to 15 April) of 1977-78. The independent variables were the minimum temperature, amount and duration of rain, wind speed, direction and persistence, humidity and the previous day's SO₂ concentration (see Table 5b). (b) Observed vs predicted SO₂ daily concentrations for Athens in the cold period of 1978-79. The predicted values were obtained by a linear multiple regression model with coefficients calculated for 1977-78 meteorological data.

ground-based inversion, which is known (Lalas et al., 1979) to be substantially increased on episode days.

Linear and non-linear multiple regression analyses have been carried out for some of the other stations, and the results are similar with regard both to the overall correlation coefficients and to the individual contributions of the meteorological variables, as one would expect in view of the relatively high correlation between stations. The differences between stations, especially between 153 and the others, that appear in the correlations of Table 2 and in the monthly time series presented in Fig. 3, are present here as well.

The predictive success of the linear multiple regression model is shown in Fig. 6(b), where the daily winter 1978–1979 concentrations calculated using the previous (1977–1978) winter's coefficients from Table 5(b) are plotted vs the measured ones. The correlation coefficient between predicted and observed SO₂ daily concentrations is 0.74 with a standard error of 27.8, both satisfactory values in view of the fact that source strength variation has not been taken into account.

Finally, a few remarks may be in order regarding the high concentrations measured in the winter of 1974–1975 and to a lesser extent in the winter of 1975–1976. The values in Table 5(b) show the primary importance of the minimum temperature and the wind speed and the secondary importance of the amount of rain, the wind direction and the wind persistence in predicting winter pollution values. Thus, it is not surprising that the winter (December, January and February), with the lowest combination of wind speed average, minimum temperature, and duration of rain (1974–1975), as shown in Fig. 4, had the highest average concentration. The winter with the next highest concentration (1975–1976) had equally low wind speed and rain duration but was warmer by 2° C. By contrast the winter of 1977–1978, which had the lowest concentrations, had double the amount of rain and a wind speed twice as high.

6. CONDITIONS FOR HIGH POLLUTION LEVELS

In this section, the conditions most likely to produce high pollution concentration episodes are examined, and a method for predicting their occurrence is presented. For the purpose of this investigation we define a pollution episode as the occurrence of a daily value larger than $250 \,\mu g \, m^{-3}$ of SO₂ in at least one station for two or more consecutive days. During the 1974–1979 period there were 42 such episodes. Analysis revealed that in all these cases, Greece was under a stationary high-pressure system, a situation known (Holzworth, 1972; McCormick, 1976) to produce light winds accompanied by night-time radiation as well as subsidence cooling, which enhance the stability of the air near the ground.

Of the 42, 26 episodes took place with cold core

highs, and these were the most persistent, lasting on average five days. The high pressure systems move into the area from either Central Europe via the Balkan Peninsula or from Western Asia. For these synoptic conditions episodes end either when a cold front, usually associated with a low pressure system from the Central or Western Mediterranean, passes through Athens or when, in a few instances, a low pressure center develops in the Eastern Mediterranean, which in combination with the high induces a N-NE flow that ventilates the Athens basin.

The rest of the cases (16 out of a total of 42) were caused by a warm-core high, which moved into the area from the southwestern Mediterranean or North Africa. The duration of such episodes is approx. 3 days, and their termination is brought about by the passage of a cold front from the west or northwest or again by the development of a low in the Eastern Mediterranean. High concentrations during the summer period, which occur despite the lack of space heating contribution to the area sources, are all of this type, i.e., the result of a warm-core high whose influence ends by the formation of a low in the Eastern Mediterranean or the Aegean Sea.

An examination of the meteorological conditions for pollution episodes shows that the minimum temperature is substantially lower as are the wind speed and amount of rain. As a matter of fact, no episode occurred with a daily average wind speed larger than 1.5 m s^{-1} , and only two episodes occurred with daily rain duration greater than 1 h. Attempts to predict episode concentrations from the meteorological data by linear and non-linear regression methods resulted in adequate but not entirely satisfactory results since again the mixing heights were not included; without them, the shortcomings of the regression models in predicting the exact magnitude of the concentration already pointed out become more pronounced.

An alternate approach, which may be of greater value in policy decisions to reduce pollution, is the prediction of episode days, i.e., days with concentration higher than a certain value. Discriminant analysis (Glahn, 1968; Green, 1978) was performed on the SO₂ data from station 151 with daily SO₂ concentrations of less than $100 \,\mu g \, m^{-3}$ assigned the value 3; between 100 and 250 $\mu g \, m^{-3}$ assigned the value 2;

between 250 and $350 \,\mu g \,m^{-3}$ the value 1; and greater than $350 \,\mu g \,m^{-3}$, the value 0. To study the relationship between these groups and construct a basis for the classification of cases among them, discriminant functions, which are linear composites of the data chosen to maximize the variance between different groups relative to the variance within groups and to be linearly independent, were calculated.

Examination of the standardized canonical discriminant function coefficients indicates that the discriminant function for separating group 0 from group 1 is dominated by the SO₂ concentrations of the previous day and the minimum temperature; that for separating group 1 from group 2, by the wind direction, the relative humidity, and the minimum temperature; and that for separating group 2 from group 3, by the duration of rain, the wind speed, the wind direction and the relative humidity. The wind direction coefficient is different in the last two functions and gives emphasis to the NE-SW direction for discriminating between groups 1 and 2 and the NW-SE for groups 2 and 3. The results for the prediction of whether the next day will be an episode day or not are shown in Table 7. A two-group analysis (below or above $250 \,\mu g \,m^{-3}$) gives identical results to what one would obtain by summing, in Table 7, Group 0 with 1 and Group 3 with 4 (except for two marginal cases out of a total of 2158). It is encouraging to note that no actual severe episode day (SO₂ greater than $350 \,\mu \text{g m}^{-3}$) was forecast to be clean (SO₂ less than $100 \,\mu g \,m^{-3}$), while on only three days out of 2158 the forecast high pollution levels (SO₂ greater than $350 \,\mu g \,m^{-3}$) failed to materialize. This suggests that the discriminant functions derived are of some value in policy decisions.

Table 8 displays four unstandardized classification functions generated from the discriminant functions which may be used in practice to forecast the group membership of the next day's SO₂ concentration. The next day's forecast values for the meteorological parameters and today's SO₂ concentration are multiplied by the corresponding coefficients and summed for each of the classification functions, and then tomorrow's SO₂ group membership is forecast to fall into the group with the highest classification score. This is the analysis technique used to construct Table 7, where the data used to construct the discriminant

Table 7. Predicted vs actual group membership of SO_2 pollution concentration in terms of today's meteorology and previous day's SO_2 value for station 151

| | - | | | | | | |
|---------------------|-------|--|--------------|------------|----------------|--------------|-------------|
| | Group | SO ₂ conc. Range | No. of cases | Predi 0 | cted grou 1 | ip memb 2 | ership 3 |
| Actual | 0 | $> 350 \mu g m^{-3}$ | 37 | 20 | 9 | 8 | 0 |
| Group Membership | 2 | $\mu g m^{-3}$ 100–250 | 36 | 12 | 10 | 14 | 0 |
| | 3 | $\mu g m^{-3}$ < 100 $\mu g m^{-3}$ | 508 1577 | 13 3 | 47 5 | 314 333 | 134 1236 |
| Total | | | 2158 | | | | |

Percentage of correctly classified cases = (20 + 10 + 314 + 1236)/2158 = 73 %.

| Group | $0 \text{ SO}_2 > 350 \mu\text{g}\text{m}^{-3}$ | 1 350–250 | 2 250–100 | 3 SO ₂ < 100 |
|--|---|-----------------|-----------------|----------------------------|
| Today's SO ₂ (µg m ⁻³) Tomorrow's forecast met. variables | 0.0122 | 0.0921 | 0.0455 | 0.0294 |
| Amount of rain (mm) | - 0.164 | 0.0165 | -0.216 | -0.199 |
| Duration of rain (h) | - 1.045 | 1.080 | -0.922 | -0.921 |
| Min. temperature (°C) | 1.551 | 1.637 | 1.823 | 1.952 |
| Wind speed $(m s^{-1})$ | 0.390 | 0.452 | 0.696 | 1.061 |
| NE wind direction* NW wind direction* Wind persistence (0-10) | 2.530 11.288 1.795 | 2.384 12.702 | 2.130 11.939 | 2.468 12.116 1.929 |
| Relative humidity $(\frac{n}{20})$ | 1.070 | 1.112 | 1.128 | 1.173 |
| Constant | - 72.98 | - 72.38 | - 65.47 | - 70.20 |

Table 8. Four sets of unstandardized classification function coefficients which may be used to predict which group tomorrow's SO₂ concentration will fall in, based on today's SO₂ value and tomorrow's forecast meteorology

* The NE and NW wind directions are as defined in Table 3.

Membership is in the group with the highest classification score calculated as the sum of the products of the measured data and the corresponding coefficients tabulated below.

functions are classified. In this calculation, the next day's meteorological measurements were used as if these values had been forecast on the previous day. These classification functions are applicable to Athens as long as there are no major systematic changes in the SO_2 emission inventory.

7. SOME CONCLUDING REMARKS

Summarizing this first analysis of the SO_2 pollution in Athens, the following conclusions can be stated.

- (i) The pollution concentration levels respond to changes in the meteorological variables in the manner expected from the general literature. Thus, the wind speed, minimum temperature and amount of rain are found to be determinant in the cold period of the year, and wind speed, wind direction and relative humidity, which are closely related, are central in the warm period.
- (ii) The SO₂ levels at most stations in the Athens basin are well intercorrelated, with differences, where they exist, explainable by the influence of local sources or geographic peculiarities.
- (iii) Multiple linear and non-linear regression models that are presented here have been able to explain a substantial part of the data variance (50-60%) and have achieved acceptable correlation coefficients.
- (iv) The synoptic situations that bring pollution episodes, i.e., high pressure systems from the north and the southwest, have been analyzed and classified, so that the forecasting of the onset as well as the end of episodes becomes feasible.
- (v) Discriminant functions have been identified which, utilizing forecasts of meteorological variables, are able to ascertain accurately whether an episode will occur the next day or not (see Table 8).

Even though the overall patterns are clear, several aspects remain to be investigated. Correlations, linear and non-linear, can improve if data on the boundary layer structure are available for inclusion in the regression analysis and if additional information on source strength variation is incorporated. This will require a reliable and detailed source inventory, without which numerical models cannot be effectively implemented or validated, nor can the spatial distribution become clearer. In addition the investigation of the impact of specific sources and policy alternatives requires knowledge of the local flow fields which are indeed complex, since they are a combination of sea breeze, heat island, high topographic relief, and variable surface roughness. Work is currently in progress on these problems which, it is hoped, will assist in describing in more detail the transport, dispersion, and deposition in the Athens basin not only of SO, and the closely related acid rain but also of other pollutants, such as ozone, whose concentrations have lately reached very high levels.

Acknowledgements—We would like to thank the Environmental Monitoring and Protection Bureau of the Greek Ministry of Social Services for providing us with their daily SO_2 measurements for Athens, and Colorado College for the use of its computing facilities. One of us (VRV) thanks the Advanced Study Program of the National Center for Atmospheric Research for support as a Senior Fellow during the period when this work was initiated. Finally we would like to acknowledge the assistance given to us by the personnel of the Meteorological Institute of the National Observatory of Athens.

REFERENCES

- Asimakopoulos D. N., Deligiorgi D. and Lalas D. P. (1980) Acoustic radar observations of the atmospheric boundary layer from the top of a steep mountain. J. appl. Met. 19, 109-112.
- Barnes R. A. (1976) Long-term mean concentrations of

atmospheric smoke and sulphur dioxide in country areas of England and Wales. Atmospheric Environment 10, 619-631.

- Benarie M., Badellon D., Menard T. and Normat A. (1974) The use of multiple regression equations for the assessment and short-term forecasting of urban area background pollution in Rouen, France, pp. 249–273. In Statistical and Mathematical Aspects of Pollution Problems (Ed. by Pratt J. W.). Dekker, New York.
- Finzi G., Zannetti P., Fronza G. and Rinaldi S. (1979) Real time prediction of SO₂ concentration in the Venezian Lagoon area. Atmospheric Environment 13, 1249-1255.
- Glahn H. R. (1968) Canonical correlation and its relationship to discriminant analysis and multiple regression. J. atmos. Sci. 25, 23-31.
- Green P. E. (1978) Analyzing Multivariate Data, The Dryden Press, Hinsdale, Illinois.
- Haagenson P. L. (1979) Meteorological and climatological factors affecting Denver air quality. Atmospheric Environment 13, 79-85.
- Holzworth G. C. (1972) Vertical temperature structure during the 1966 Thanksgiving week air pollution episode in New York. Mon. Weath. Rev. 100, 625-633.
- Interim Technical Report (1975). Vol. IV, Environmental Monitoring and Protection Bureau, Greek Ministry of Social Services, Athens.
- Jensen N. O. and Peterson E. W. (1978) On the escarpment wind profile. Q. Jl R. met. Soc. 104, 719-728.
- Karapiperis L. and Catsoulis V. (1977) Contribution to the study of sea breeze in the Athens area in the winter. Bull. Greek Met. Soc. 2, 4-17.
- Lalas D. P., Karras G. S. and Zikos P. I. (1979) Conditions for increased SO₂ pollution concentration in Athens, Greece.

Report to the Ministry of Social Services, Dept. of Meteorology, University of Athens, (in Greek).

- McCormick R. A. (1976) Air pollution climatology. In Air Pollution. (Ed. by Stern A. C.), Vol. I, Academic Press, New York.
- Metaxas D. A. (1977) The interannual variability of the Etesian frequency as a response of atmospheric circulation anomalies. Tech. Report No. 109, Univ. of Ioannina, Greece.
- Peterson J. T. (1972) Calculation of SO₂ concentrations over metropolitan St. Louis. Atmospheric Environment 6, 433-442.
- Proceedings of the 2nd International Symposium on the Deterioration of Building Stone, Athens, September, 1976.
- Shir C. C. and Shieh L. J. (1974) A generalized urban air pollution model and its application to the study of SO₂ distribution in the St. Louis metropolitan area. J. appl. Met. 13, 185-204.
- Taylor P. A. (1969) The planetary boundary layer above a change in surface roughness. J. atmos. Sci. 29, 432-440.
- Tiao G. C., Box G. E. P. and Hamming W. J. (1975) A statistical analysis of the Los Angeles ambient carbon monoxide data 1955–1972. J. Air Pollut. Control Ass. 25, 1129–1136.
- Vermeule E. (1977) The Parthenon is shrinking. Atlantic Monthly 239, 82-85.
- Weather in the Mediterranean (1965), pp. 65-70. British Meteorological Office, H. B. M. Stationery Office, London.
- Yocom J. and Upham J. (1978) Effects of the air pollution on economic materials and structures. In *Air Pollution*, (Ed. by Stern A. C.), Vol. II, Academic Press, New York.
- Yocom J. E. (1979) Air pollution damage to buildings on the Acropolis. J. Air Pollut. Control Ass. 29, 333-338.