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DIURNAL CONCENTRATIONS OF BLACK CARBON AND SOME OTHER AIR POLLUTANTS IN LJUBLJANA, YUGOSLAVIA

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Abstract - We report on measurements from an automated air pollution and meteorological station operating in the city center of Ljubljana, Yugoslavia. Aerosol black carbon, SO_2, NO and NO_2 were measured continuously on a 30-minute timebase. Filter samples integrated over periods of from one to three days were analyzed for total particulate carbon and sulfur species. Large variations of pollutant concentrations were seen, correlating with emission source activity and periods of meteorological stagnation. Correlations between primary (BC) and secondary (S_P) species were seen, suggesting a rapid SO2 to sulfate conversion mechanism. We discuss the influence of meteorology and primary emission activity on air quality in the city.

Key word index: Diurnal concentration, aerosol black carbon, gaseous pollutants

INTRODUCTION

Ljubljana is a city of approximately 300,000 inhabitants located in a basin surrounded on three sides by hills and mountains. Wintertime temperature inversions frequently cause episodes of fog accompanied by high levels of air pollution. There are many scattered and uncontrolled coal burning stoves used for space heating, which are responsible for large emissions of soot, SO_2, and other pollutants (Bizjak *et al.*, 1988). Two large power plants burning gas and coal are also important sources, although their stacks are high enough (100 and 150 m) so that during episodes with low inversion heights, their emissions may be released above the inversion and thus not always contribute to the local ground-level air pollution. Traffic emissions are an additional source of particulate matter and gaseous pollutants.

An automated air pollution monitoring station is installed in the city center measuring half hour average concentration of SO_2, NO, NO_2, NO_X, as well as general meteorological parameters (temperature, relative humidity, wind speed and direction). An aethalometer (Hansen, 1982) was installed recently to measure the concentration of aerosol "black" carbon (BC) by an optical attenuation method on quartz fibre filters. In this work we present some results of diurnal BC and other pollutants measured from September 1990 to February 1991 in the center of Ljubljana.

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EXPERIMENTAL

Sampling

The sampling site is located in a square in the city center of Ljubljana, some 40 meters from the main street. The instrumentation installed in the ANAS automated environmental monitoring station includes: two aethalometers (one commercial, one of KIBK manufacture); fluorescent SO_2 analyzer; NO_X analyzer; gas calibrator; and meteorological equipment (T_A, %RH, wind speed and direction). The equipment is connected to a data acquisition and control system on-line to the central computer of the Meteorology Institute of Slovenia. All instruments operated on a 30 minute measuring timebase.

Analysis

The aethalometers produce deposits on quartz fiber filters representing aerosol samples integrated over periods of from 6 to 24 hours. These samples were analyzed by an optical transmissometer, constructed at KIBK, Ljubljana, as a check on the total amount of aerosol black carbon (Gundel *et al.*, 1984). Total particulate carbon and sulphur (C_P, S_P) were determined by combustion of the filters in oxygen followed by conductometric detection of CO_2 and SO_2.

RESULTS AND DISCUSSION

Aerosol black carbon concentrations were measured continuously on a 30 minute timebase from September 1990 to February 1991 with only a few short interruptions. The values ranged from less than 0.1 $\mu g\ m^{-3}$ (limit of detection) during periods of good air mixing in the valley, to about 40 $\mu g\ m^{-3}$ during high pollution episodes accompanied by low wind speed, temperature-inversions and fog. Figure 1 shows a typical example of diurnal BC, SO_2, NO, NO_2 and weather data (T, RH, wind speed and direction) variations for the period December 1 – 7, 1990. We conclude that in general, temporal BC variations coincide well with SO_2 and NO concentrations and slightly less well with NO_2 concentrations. However, there are some short periods when good correlation is not seen. This may be due to the complexity of emission sources and partial prevalence of particular sources during certain measuring periods. The effect of meteorology is also obvious. During this period, weather conditions were typical for winter: temperature around 0° C, prevailing low-wind periods with changes in direction and speed. The relative humidity was high during the first part of period and lower during the second part. A close examination of the results show that some SO_2 peaks were not accompanied by BC maxima (e.g., hours 12 – 20 on Dec. 1, hours 00 – 04 on Dec. 2). Peaks in SO_2 and NO concentrations coincide well. NO and NO_2 profiles sometimes differ, possibly due to the reaction of NO with oxidants. Unfortunately, ozone data are not available during this measuring period so that estimates of the effects of photochemical oxidants can not be made. The temporal correlations of pollution species mentioned above leads to a general conclusion about the similarity of emission sources in the city center. Automobile exhaust is probably the most important source of BC and NO_X. The high concentration of SO_2 is probably due to coal burning; traffic

alone can not contribute such an amount of SO_2. The one-hour maximum concentration standards in Slovenia are 350 μg m^{-3} for SO_2 and 200 μg m^{-3} for NO_2. These limits were exceeded during winter 1990/1991 several times, for example on Dec. 5, 1990 as shown in Fig. 1 (b and d).

Good correlations between the concentrations of primary air pollutants (BC, C_P in Fig. 2) emitted from the same sources can be easily understood. In addition, a relatively good correlation ($r = 0.7$) was obtained for total BC and S_P (sulphate) determined on the aethalometer filters, as shown in Fig. 3. Particulate sulphur is present in the urban air mostly in the form of sulphate, a secondary air pollution species. The fact that a secondary pollutant (sulphate) follows a primary one (BC) so closely can have at least two interpretations: first, that SO_2 oxidation occurs immediately after combustion, and second, that BC (soot) plays an important role in the sulphate formation mechanism as a potential catalytic species in the atmosphere. Previous work has shown that SO_2-to-sulphate conversion is a complex mechanism involving oxygen, primary oxidants from combustion, the effects of various catalytic species, competition and synergism between reactions depending upon other conditions such as temperature, availability of liquid water, etc. (Seinfeld, 1986, Middleton and Kiang, 1978, Grgic *et. al.*, 1991).

CONCLUSIONS

The combination of physical and chemical measurements with meteorological data show the contribution of local emissions from combustion, space heating and traffic to the overall level of air pollution in Ljubljana. The good correlation between pollution species indicate a commonality of emission sources. The influence of meteorology is very great: episodes of high concentration correlate well with conditions of stagnation and temperature-inversion. Diurnal variations show great differences between the lowest and highest average half-hour concentrations. Maxima often exceed the accepted concentration standards for Slovenia (SO_2: 350 μg m^{-3}, NO_2: 200 μg m^{-3}), leading to possible impacts on public health. These concentrations show a strong seasonal variation, with large differences between non-heating and winter heating season for all pollution species.

The temporal correlation of the concentration of BC, C_P (primary combustion species) and S_P (secondary species) suggest a rapid SO_2 to sulphate conversion mechanism. We conclude that heterogeneous SO_2 oxidation in aqueous phase (fog, wet aerosols) involving primary oxidants, catalysts, metal ions, etc may be important in the atmosphere in this city. Since similar conditions are believed to exist in other areas of Eastern Europe, this finding may be of importance for environmental quality in the region.

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FIGURE CAPTIONS

Fig. 1 Diurnal 30 min average concentration of BC (a), SO_2 (b), NO (c) and NO_2 (d) and meteorological data (e and f), Dec. 1 – 7, 1990.

Fig. 2 Analysis of aethalometer filters collected from Sept. 1990 to Feb. 1991. Line traces (left axis)—carbon concentrations: (+) points, aerosol black carbon (BC); (o) points, total particulate carbon (C_P). Vertical bars (right axis)—total particulate sulfur (S_P).

Fig. 3 S_P vs. BC concentration (aethalometer filters), Sept. 1990 to Feb. 1991.

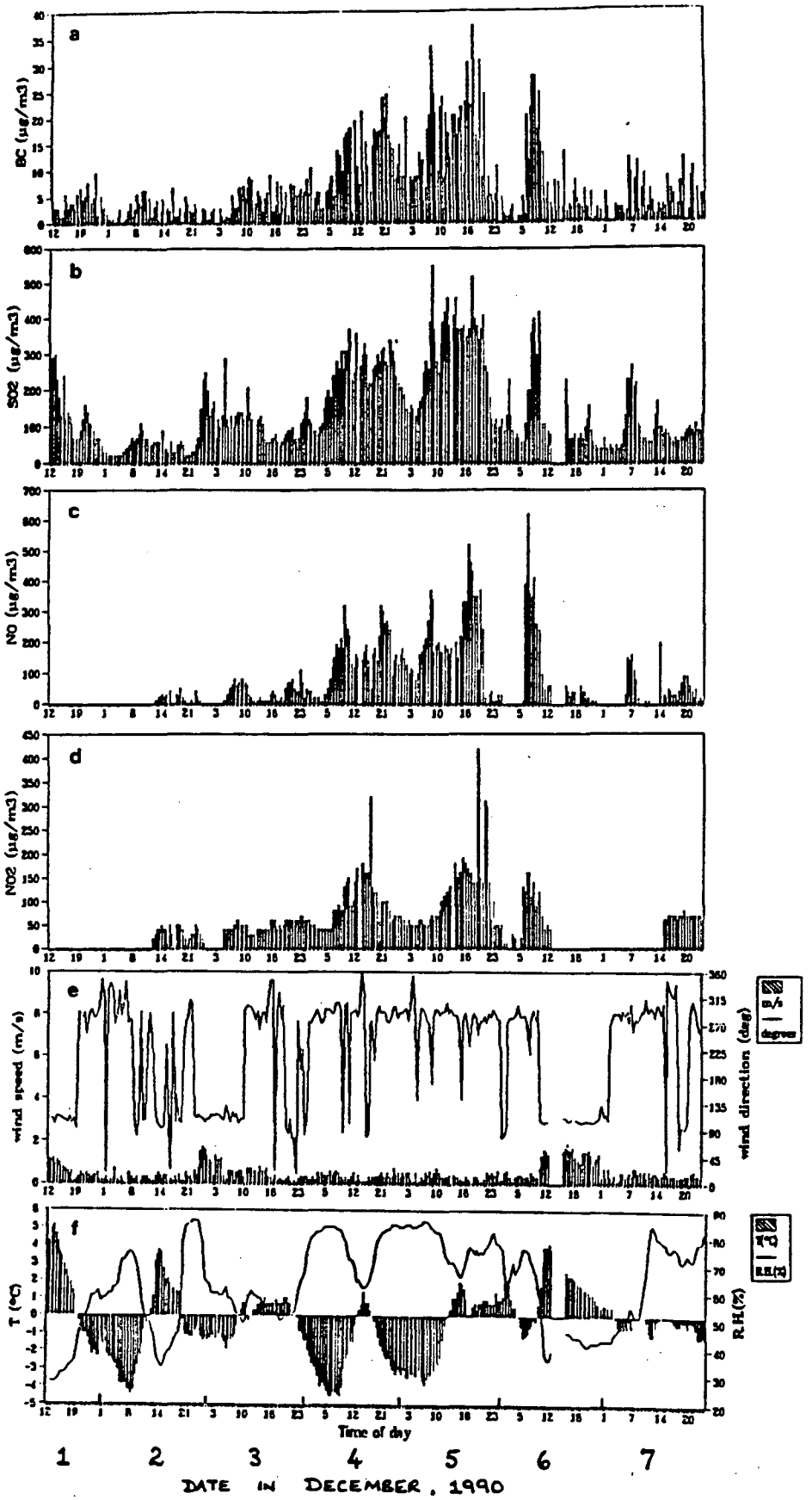
a
BC (µg/m3)
b
SO2 (µg/m3)
c
NO (µg/m3)
d
NO2 (µg/m3)
e
wind speed (m/s)
wind direction (deg)
m/s
degrees
f
T (°C)
R.H.(%)
Time of day
1 2 3 4 5 6 7
DATE IN DECEMBER, 1990

Figure 1

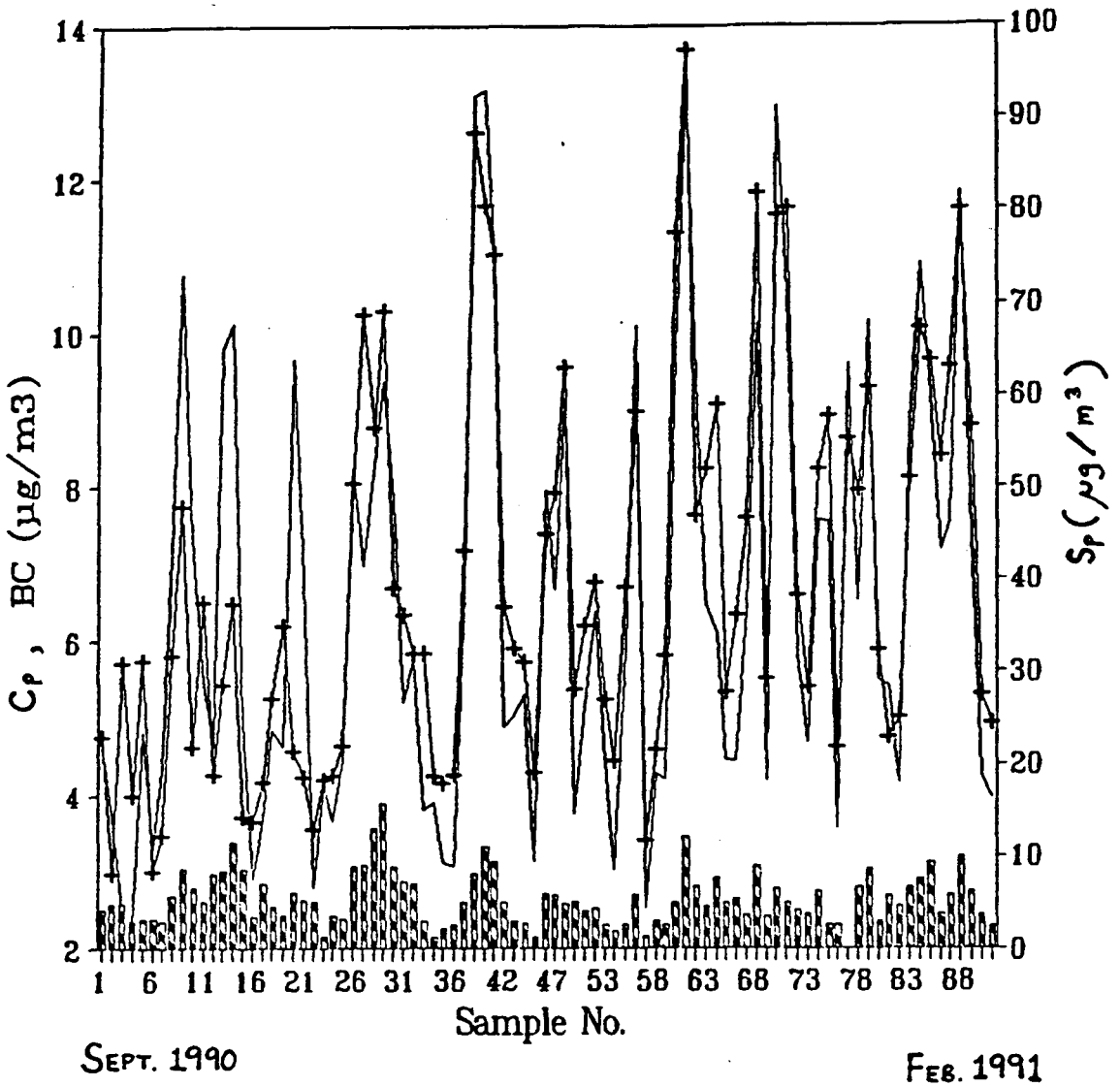
14
12
10
8
6
4
2
100
90
80
70
60
50
40
30
20
10
0
Cp , BC (µg/m3)
Sp (µg/m³)
1 6 11 16 21 26 31 36 42 47 53 58 63 68 73 78 83 88
Sample No.
Sept. 1990
Feb. 1991

Figure 2

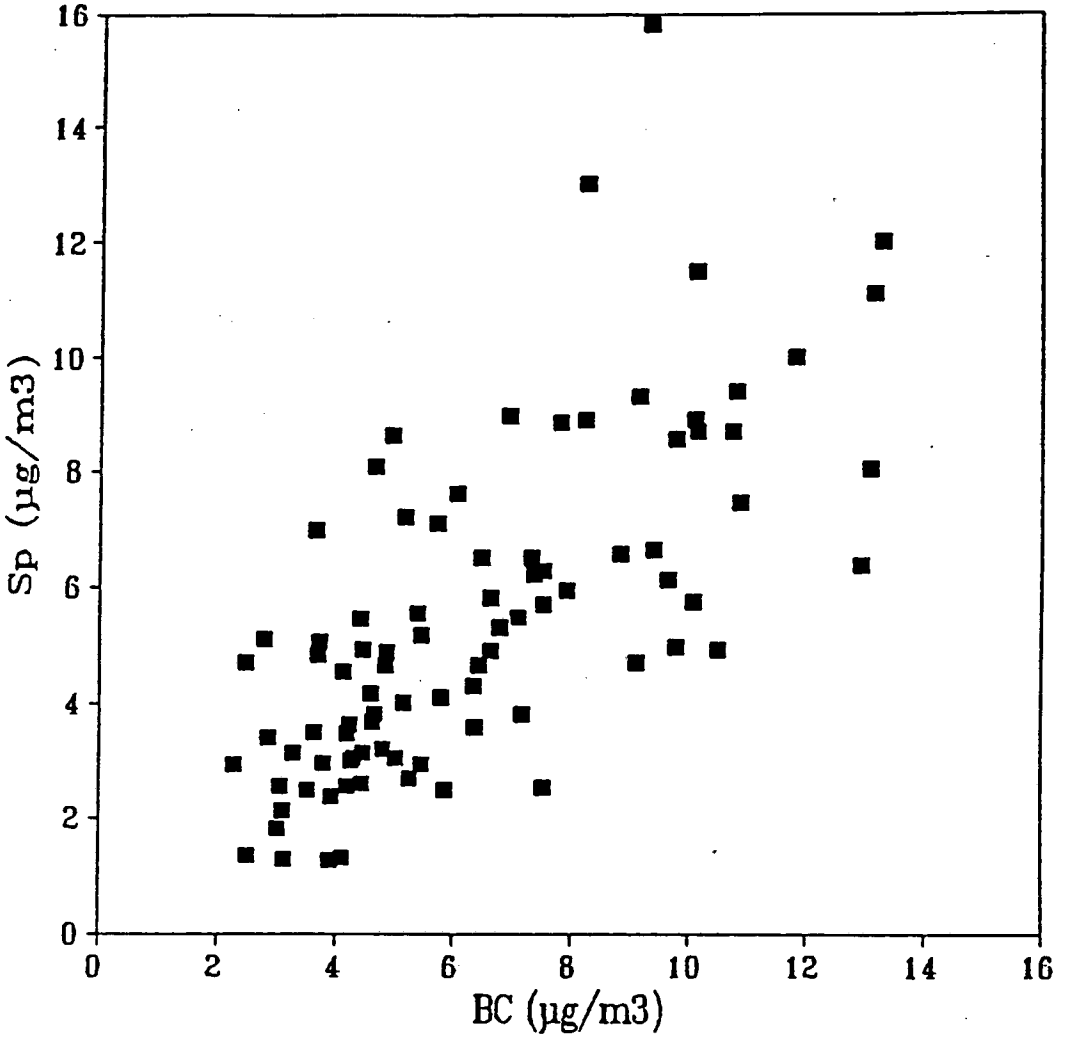

Figure 3

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