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DIURNAL CYCLE OF SO_2 CONCENTRATIONS IN RIJEKA AND ITS RELATION TO MAXIMUM AND AVERAGE DAILY CONCENTRATIONS

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Continuous recording of SO_2 concentrations at one site in Rijeka in the heating season has shown that in spite of geographic and climatic differences, the pattern of diurnal cycle of SO_2 concentrations does not differ from that recorded in Zagreb and in other towns with a temperate climate. The pattern is characterized by two peaks: a higher one in the morning that represents daily maximum and a lower one in the afternoon that is a good approximation of daily mean. Accordingly, maximum and mean daily concentrations could be assessed by short-term samples collected over given periods (8–10 and 15–18 h). As the diurnal cycle of SO_2 concentrations could be disturbed by changes in weather conditions, equations were developed and coefficients established for calculating correction factors for adjustment of the estimated daily maximum and mean concentrations from two samples of short duration. The equations developed in Zagreb proved to be also valid for Rijeka. Presumably, the procedure could be used in other towns in the temperate region after the pattern of diurnal cycle of SO_2 concentrations has been verified and the coefficients necessary for calculating correction factors established.

Key terms:
air pollution, daily maximum, heating season, mean daily concentration, temperate climate, urban area

Some time ago a method was proposed by *Wilder and co-workers* (1) for estimating maximum and mean daily SO_2 concentrations from two samples of short duration. It was based on the analysis of diurnal cycles of SO_2 concentrations in the central part of Zagreb during the heating season. The analysis showed that on days with a typical diurnal SO_2 concentration pattern there was a time interval in the morning when the concentration was in good correlation with the daily maximum and a time interval in the afternoon when the concentration was a fair approximation of the daily mean. The pattern, which was the result of the daily human activity cycle and of the daily cycle of air turbulence, could be disturbed by changes in meteorological situation. Further analysis of the results and their relationship, however, showed that from the ratio of measured SO_2 concentrations over the selected morning and afternoon intervals, coefficients could be determined for calculation of correction factors by which the estimated maximum and average values could be adjusted in order to obtain a better approximation of the true values. The method was verified four years later at the same site, after the SO_2 concentrations had dropped considerably, and was found to be still valid (2). As the factors were based on the results from one site in one city it could only be anticipated that a similar relationship would hold for other cities with temperate climate, taking account of the fact that the optimal sampling time and numerical values of the coefficients may be different. Therefore the results of continuous SO_2 recording in Rijeka (3), a coastal town with the geographic position and climatic characteristics different from those of Zagreb have been used to test the described approach. It is worth mentioning that unlike in continental towns the annual cycle of SO_2 concentrations in Rijeka shows in addition to a winter maximum, another, although lower maximum in summer. That maximum is evidently caused by tourist activities, but need not necessarily influence the relations within the diurnal cycle.

EXPERIMENTAL

Description of location

Rijeka is situated at the north of Kvarner bay along the narrow coastal line and at the slopes of mountains which form a barrier between the Adriatic coast and the hinterland. According to the 1981 census Rijeka had 193.000 inhabitants. The climate is temperate mediterranean. Major air pollution sources are two oil refineries, a power plant and a coke plant (Figure 1).

Equipment, measurement programme and sampling site

Philips coulometric SO_2 monitor PW 9700, sensitivity: 10 μg SO_2 per cubic metre of air, accuracy: 2%, response time: 95% in three minutes was used in the survey.

Continuous measurements were carried out for over five weeks in the heating season (January/February). The instrument was situated in a public building in a residential and business district of the central part of Rijeka near the railway station and port close to a busy road and not far from an oil refinery. The entrance opening of the instrument was eight metres above the ground level.

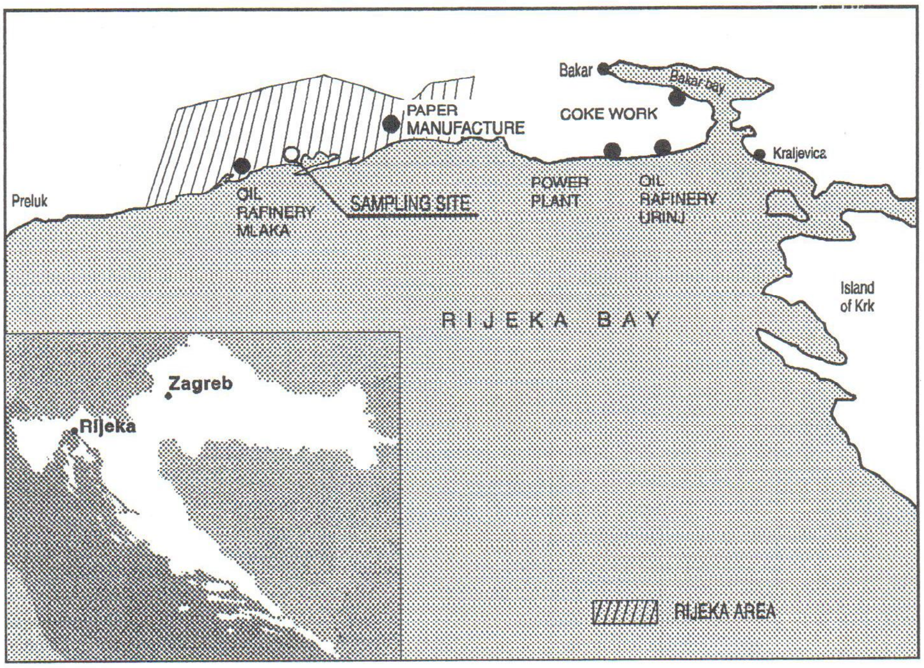

Figure 1 *Sampling site (o) and major sources of SO_2 emissions (•) in the Rijeka bay area*
Locations of Rijeka and Zagreb on the map of Croatia

RESULTS AND DISCUSSION

Summarized results of the measured SO_2 concentrations by days expressed as 24 h, 1 h and 30 min average concentrations are shown in Table 1.

Table 1 Summarized results of SO_2 measurement ($\mu g/m^3$)

Averaging period	n	$\overline{C}$	Range
24 hours	34	221	37–516
1 hour	734	221	10-1090
30 min	1518	221	10–1256

n – number of data, $\overline{C}$ – arithmetic mean

Diurnal cycles of SO_2 concentrations

The average diurnal cycle over the total period of measurement was constructed of 1 h SO_2 concentrations, expressed in terms of the corresponding 24 h average, following the relation

$$C_{i,i+1} = \frac{\sum_{j=1}^{34} \frac{C_{ij}}{C_j}}{N} \qquad /1/$$

where:
$C_{i,\,i+1}$ – average relative concentration between i^{th} and $i+1^{th}$ hour,
N – number of days when measurement took place,
C_{ij} – average concentration between i^{th} and $i+1^{th}$ hour of day j,
C_j – daily mean concentration on day j.

The indices may acquire the following values:
$1 \le j \le 34 \qquad 0 \le i \le 23$

Figure 2 shows the average diurnal cycle in Rijeka as compared to the diurnal cycle for Zagreb. There is no marked difference in the pattern of diurnal cycles of the two cities. The SO_2 concentration starts rising at about 6.00 a.m., reaching a maximum between 8.00 and 11.00 a.m. After that the concentration diminishes and rises again after 16.00 hours. The afternoon maximum is reached between 17.00 and 19.00 hours. The afternoon maximum is close to the daily mean concentration.

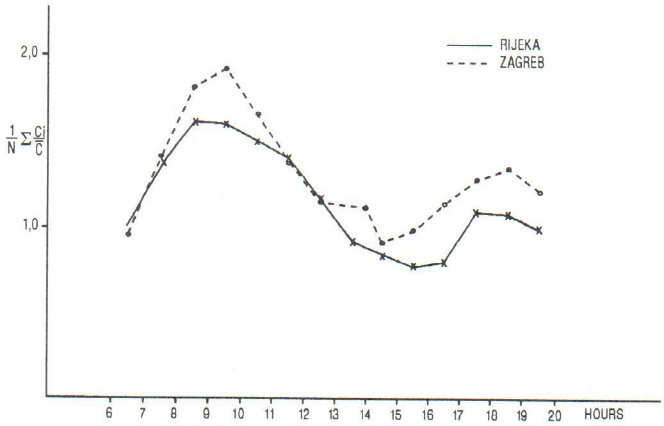

Figure 2 *Mean diurnal SO_2 concentration pattern for winter in Rijeka and Zagreb*

Thirty-minute maximum to daily average SO_2 concentration ratio

The ratio of 30-min maxima to daily average SO_2 concentrations calculated for the period of measurement of 34 days varied in the range from 1.49 to 4.31. The mean ratio of 30-min maxima to daily mean SO_2 concentrations in Rijeka (2.6) is very near the value of 2.4 mentioned in the literature (4, 5) and does not greatly differ from the average ratio for the city of Zagreb 2.1 (6). Therefore it can serve for a rough approximation of probable maximum 30-min concentrations when only daily averages are measured.

Estimation of daily maximum and average concentrations

According to *Wilder and co-workers* (1) the first step was to find optimal sampling periods and determine concentrations which are close to maximum and average daily concentrations under stable atmospheric conditions. The diurnal cycle of SO_2 concentrations suggests that the same intervals found by Wilder and co-workers as the most suitable for Zagreb, also seem to be most suitable for Rijeka i.e. 8.00–10.00 a.m. for maximum and 15.00–18.00 p.m. for daily average concentration. To obtain correction factors for the days with a disturbed diurnal pattern, the following equations were suggested by Wilder and co-workers:

$$\log K_1 - 1 = b \log \left[\frac{C_{8-10}}{C_{15-18}} \right] + a \quad \text{for maximum concentrations} \qquad /2/$$

and

$$K_2 = 10^{\alpha} \left[\frac{C_{8-10}}{C_{15-18}} \right]^{\beta} \quad \text{for daily means} \qquad /3/$$

These were derived from analysis of the relationship between the ratio of the measured morning to afternoon concentrations and the ratio of the true to the estimated maxima. Since the diurnal cycle in Rijeka does not differ significantly from that in Zagreb, the same relations were used for calculating correction factors in Rijeka.

Daily maximum concentrations

The measured 1 h maximum concentrations were correlated with the estimated maximum values obtained by multiplying daily concentrations for the period 8.00–10.00 hours with the corresponding correction factor (K_1). The coefficients a and b calculated from the results for Rijeka where a = – 0.0563 and b = – 0.9851. The relationship of the estimated maximum daily SO_2 concentrations and the measured ones is shown for 1 h maxima in Figure 3. It can be seen that the correlation is very good ($r = 0.947$). The difference between the estimated and measured maxima is not statistically significant ($t = 0.38$, $P > 0.5$).

The attempt to calculate correction factors using the Zagreb coefficients ($a = 0.0254$ and $b = -1.0623$) was also successful. The relations between the

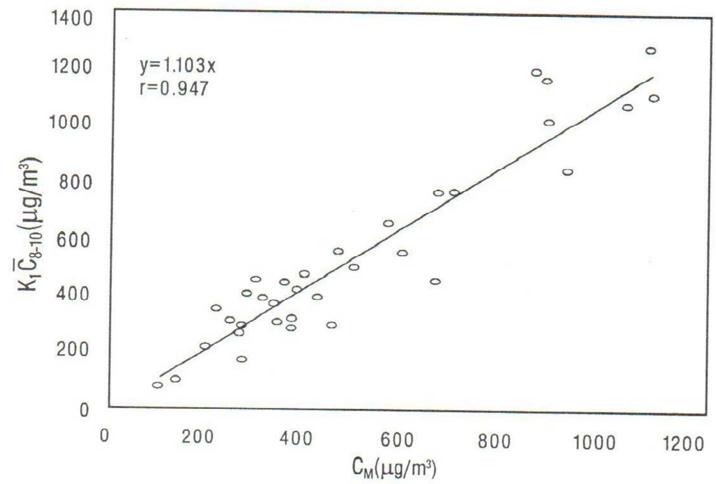

Figure 3 *Measured (C_M) vs estimated ($K_1\ \overline{C}_{8-10}$) maximum SO_2 concentrations*

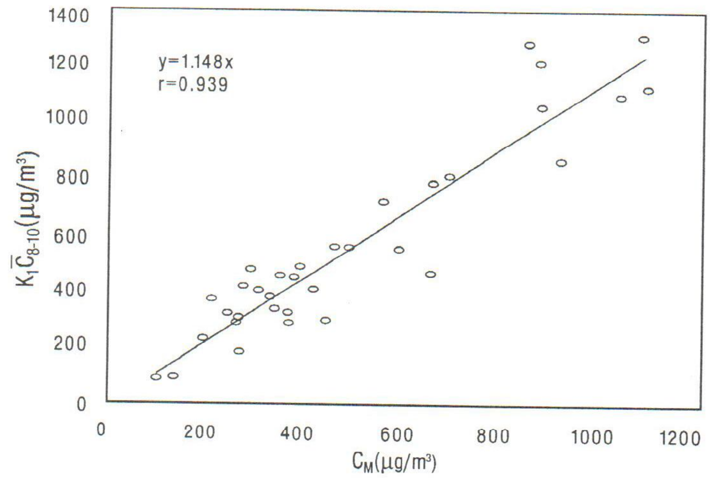

Figure 4 *Measured (C_M) vs estimated ($K_1\ \overline{C}_{8-10}$) maximum SO_2 concentrations using Zagreb coefficients*

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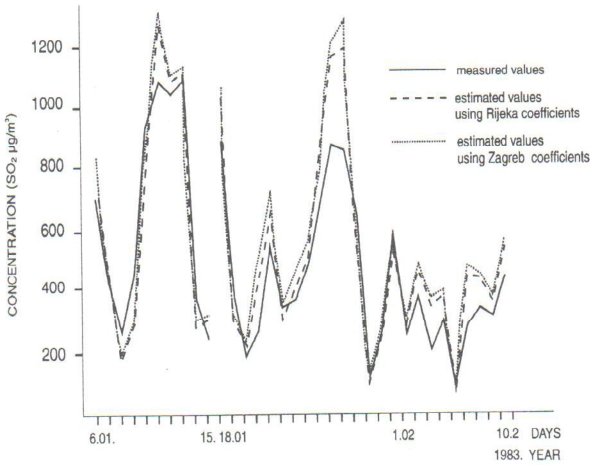

Figure 5 *Measured and estimated daily maximum SO_2 concentrations over the monitoring period*

measured 1 h maximum concentrations and those estimated using the Zagreb coefficients are shown in Figure 4. The correlation was high ($r = 0.939$). The difference between the measured and the calculated values was not statistically significant ($t = 0.792$, $P > 0.1$).

The measured and estimated maximum concentrations using both the Rijeka and the Zagreb coefficients for calculating correction factors are presented day by day in Figure 5.

Daily mean concentrations

The actual daily mean concentrations were correlated with the estimated values obtained by multiplying afternoon concentrations for the period 15.00–18.00 hours with the correction factor K_2. The coefficients for calculating K_2 based on Rijeka results were $\alpha = -0.0698$ and $\beta = 0.4831$. The relationship of the estimated and the true daily average SO_2 concentrations is shown in Figure 6. The correlation is high ($r = 0.959$) and the difference between the two sets of results is not significant ($t = 0.637$, $P > 0.5$).

Using again the Zagreb coefficients ($\alpha = -0.0857$ and $\beta = 0.3170$) for calculating correction factors a good correlation was obtained ($r = 0.925$), but the estimated concentrations were systematically lower, and the difference between the estimated and measured means (Figure 7) was statistically significant ($t = 3.785$, $P < 0.05$).

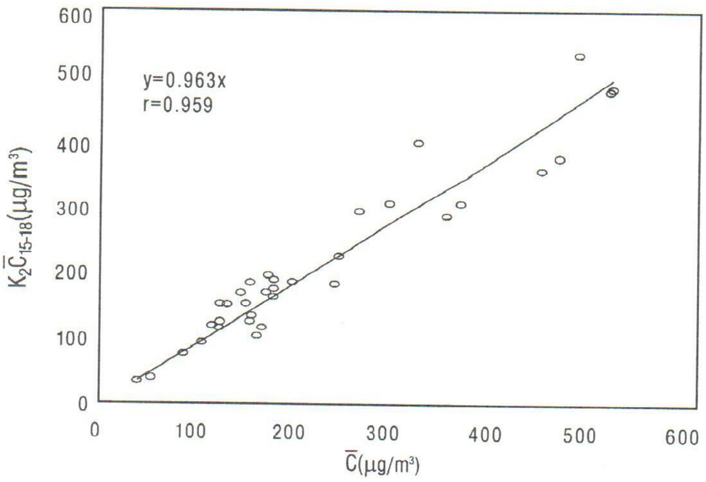

Figure 6 *Measured ($\overline{C}$) vs estimated $K_2\overline{C}_{15-18}$ daily mean SO_2 concentrations*

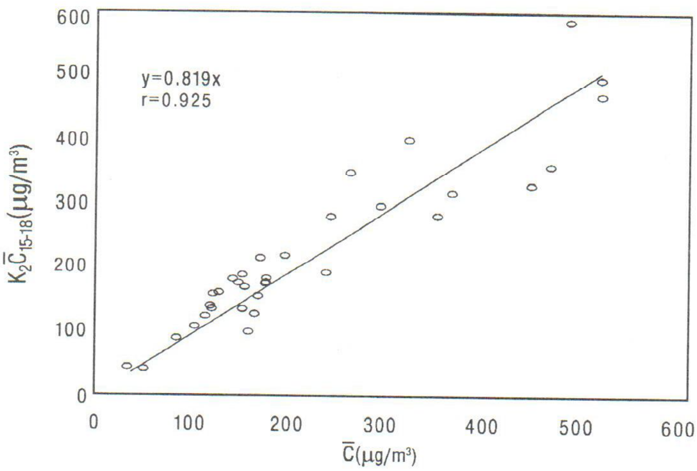

Figure 7 *Measured ($\overline{C}$) vs estimated $K_2\overline{C}_{15-18}$ daily mean SO_2 concentrations using Zagreb coefficients*

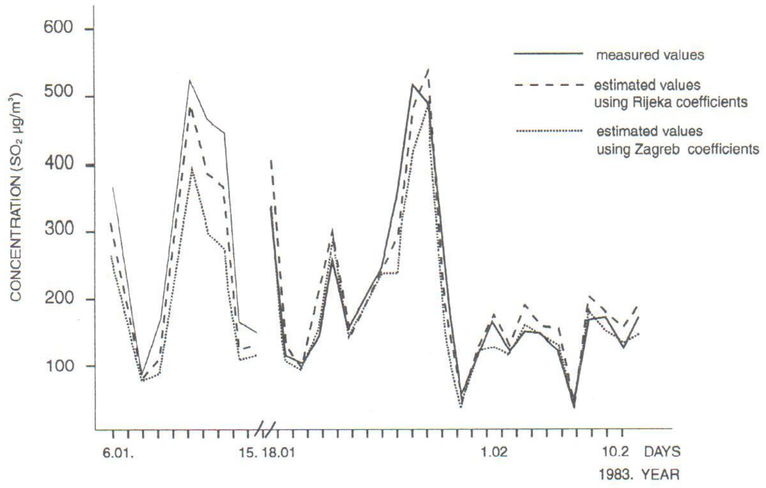

Figure 8 *Measured and estimated daily mean SO_2 concentrations over the monitoring period*

The measured and estimated daily mean concentrations using the correction factors based both on the Rijeka and the Zagreb coefficients are presented in Figure 8.

CONCLUSIONS

The analysis of SO_2 concentrations in Rijeka, obtained by continuous recording over five weeks in the heating season, has shown that the diurnal cycle of SO_2 concentrations is in good agreement with those observed in Zagreb and other towns in the regions with a temperate climate. Therefore the approach suggested by *Wilder and co-workers* (1), based on the Zagreb data, for estimating daily maximum and average concentrations from two samples of short duration, collected over given periods, proved to be applicable in Rijeka as well.

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