

## Air quality in Rijeka, Croatia

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In this paper, the hourly mean ambient concentrations of nitrogen dioxide ( $\text{NO}_2$ ), carbon monoxide (CO), hydrogen sulfide ( $\text{H}_2\text{S}$ ), sulfur dioxide ( $\text{SO}_2$ ), ozone ( $\text{O}_3$ ), benzene ( $\text{C}_6\text{H}_6$ ) and particulate matter ( $\text{PM}_{10}$ ) measured over the last 4.5 years at the two urban sites in Rijeka are analyzed. The first site is located in the center of the town, whereas the other is located in the southeastern part, closer to the industrial zone of Rijeka. The site in the center of Rijeka is subject to heavy vehicular traffic, thus exhibiting substantially higher  $\text{NO}_2$ , CO and  $\text{PM}_{10}$  concentrations; however, the other site is characterized by much higher  $\text{SO}_2$  concentration. The diurnal and annual variations in pollutant concentrations reflect the effects of both human activity and periodic variations in meteorological conditions, whereas average weekly variations differ as per the anthropogenic emissions. Finally, in accordance with the trend of decreasing pollutant concentrations since the mid-1980s,  $\text{SO}_2$  concentrations decreased at both the sites, whereas  $\text{NO}_2$  concentration decreased at the site closer to the industrial area of Rijeka.

*Keywords:* ambient concentrations, urban pollution, traffic, oil refinery, temporal variations

### 1. Introduction

The Rijeka Bay Area (RBA) is located on the eastern coast of the northern Adriatic Sea. It is one of the major industrial regions in Croatia. According to the Ministry of Environmental Protection, Physical Planning and Construction of the Republic of Croatia (MPPPC), only two individual sources, the Rijeka Oil Refinery (ROR) and the Rijeka Thermo-power Plant, are responsible for 20 % of the total Croatian emissions of sulfur dioxide ( $\text{SO}_2$ ) and 4 % of the total Croatian emissions of nitrogen oxides ( $\text{NO}_x$ ). The ROR emits 8933 tons of  $\text{SO}_2$  and 1656 tons of  $\text{NO}_2$  annually. With regard to  $\text{SO}_2$ , ROR is the major individual source in Croatia, contributing 13 % of the total Croatian emissions (in comparison, the corresponding figure for the Sisak Oil Refinery is 9 %) (MPPPC data for 2002, <http://www.mzopu.hr/>).

Until recently, the ROR operated simultaneously at two coastal locations, Mlaka and Urinj (M and U in Fig. 1). At Mlaka, one of the oldest refineries in the region, the plant started functioning in 1883. In its early days, it was located in the suburbs of Rijeka. Today, due to the growth of the town, it is part of the densely populated section of Rijeka. In recent years, elevated ambient concentrations of hydrogen sulfide ( $\text{H}_2\text{S}$ ) and  $\text{SO}_2$  in the refinery's neighborhood motivated local authorities to shut down the plant in 2008. This was followed by a surprisingly small decrease in the pollutant concentrations at the nearby monitoring site (approximately 400 m north of the refinery) (Forgić, 2010).

The other ROR plant (Urinj) is located approximately 12 km southeast of Rijeka, in the industrial area of Kostrena and Bakar (<http://www.ina.hr/default.aspx?id=58>). According to Alebić-Juretić (2008), it emits approximately 7795 tons of  $\text{SO}_2$  and 1918 tons of nitrogen dioxide ( $\text{NO}_2$ ) per year (data for 2001). In the same area, other industrial plants of the RBA are also located. In 2001, the total estimated annual anthropogenic emissions of major pollutants in the RBA were 36430 tons of  $\text{SO}_2$ , 5894 tons of  $\text{NO}_2$  and 51–316 tons of ammonia ( $\text{NH}_3$ ), respectively (Alebić-Juretić, 2008).

Due to the heavy industrialization in the RBA in the 1960s and the 1970s, Rijeka (which is also a major port of Croatia) was one of the most polluted towns of Croatia during the mid-1980s. In the last few decades, the reductions in the emissions have led to a noticeable decrease in airborne levels of  $\text{SO}_2$  and a consequent decline in the sulfate and the acidity of rainwater (Alebić-Juretić, 1995 and 2008; Čanić et al., 2009); however, nitrogenous gases did not exhibit any such decline (Alebić-Juretić, 2008). During the past 25 years, trends indicate decreasing concentrations of heavy metals in the port sediments in the Rijeka harbor (Cukrov et al., 2010).

In spite of the emission reductions, which are in accordance with the general European trends (Monks et al., 2009), incidents of severe local air pollution still occur occasionally (e.g., Prtenjak et al., 2009). These incidents are caused by a complex wind regime and other local meteorological conditions (e.g., Klaić et al., 2003; Nitis et al., 2005; Klaić et al., 2009).

Generally, the contributions of pollution sources to pollutant concentrations are evident at the local scale. However, pollutants emitted in one region can also affect distant areas because they are dispersed and submitted to advection by the airflow. A potential influence of the RBA sources on the pollutant levels at the regional scale is discussed for ozone ( $\text{O}_3$ ) in Žabkar et al. (2008).

The negative effects of air pollution on human health, such as respiratory and heart diseases, premature mortality and reduced life expectancy are widely documented (e.g., the review papers of Kampa and Castanas, 2008 and Monks et al., 2009). Additionally, pregnant women exposure to elevated  $\text{SO}_2$  concentrations can result in premature delivery and low birth weight (e.g., Mohorović, 2004). The relation of the excess mortality in Rijeka with elevated particu-

late matter ( $PM_{10}$ ) and  $O_3$  concentrations during the heat wave conditions in the summer of 2003 has been described by Alebić-Juretić et al. (2007).

Because pollutant emissions change with time for a variety of reasons (such as opening or closure of industrial plants, change in vehicular fleet, change in the fuel consumption, quality or type of fuels, etc.), it is critical that pollution levels are inspected on a regular basis. Therefore, the aim of this study is to assess the current exposure (corresponding to the last few years) of Rijeka's inhabitants to different pollutants (namely,  $NO_2$ ,  $CO$ ,  $H_2S$ ,  $SO_2$ ,  $C_6H_6$ ,  $PM_{10}$  and  $O_3$ ), and to check if the decrease in the concentration of  $SO_2$  in the town of Rijeka, which started at the end of 1980s (Alebić-Juretić, 2008), still continues. Additionally, temporal variations in pollutant concentrations at the daily, weekly and annual scales are also determined based on the experimental data.

## 2. Measuring sites and measurements

The hourly mean data measured at two urban sites in the town of Rijeka, namely, Rijeka-1 ( $45^\circ 19' 38.8''$  N,  $14^\circ 26' 47.9''$  E) and Rijeka-2 ( $45^\circ 19' 14.8''$  N,  $14^\circ 29' 0.5''$  E) during the past 4.5 years (1 January 2006–30 June 2010) were analyzed (Figure 1, top). The study sites are a part of the National Air Quality Network (NAQN) established within the framework of implementation of the air protection measures prescribed as part of the environmental impact assessment procedure for continuous monitoring. Data are available at the NAQN website (<http://zrak.mzopu.hr/>) at a temporal resolution of 1 h. However, the network website does not have any information regarding possible data quality control. (Note that the quality control of the data collected by other Croatian institutions monitoring the air quality in urban environments, namely, the Institute of Medical Research and Occupational Medicine, Zagreb and the Institute of Public Health, Rijeka are described in Mücke (2008).)

Measuring site Rijeka-1 is located in the center of the town of Rijeka (*Stari grad* quarter, *Žrtava fašizma* Street, near the crossing with *Alda Colonella* Street). From the satellite view (Google Maps), it is seen that the site is placed at the northern side of the NW-SE-oriented street canyon. The site's purpose is to record the pollution levels, which are primarily a result of vehicular traffic. Nevertheless, Rijeka-1 is also exposed to the effects of other urban/industrial sources.

Rijeka-2 is located in the southeastern part of the town (*Sušak* quarter, *Franje Belulovića* Street). According to the satellite view, it appears to be in a more open neighborhood. A few large buildings are placed on the western and the northern side of the site (roughly 70 m and 40 m away, respectively). To the south of the site, there is the *Franje Belulovića* Street, and trees are located further southwards. According to the NAQN website, it is considered to be a representative of pollution levels in both residential and industrial areas. The measured parameters are listed in Table 1. As seen in Table 1, data on  $C_6H_6$  and  $H_2S$  concentrations are frequently missing.



**Figure 1.** Upper panel: A satellite view of greater Rijeka region (source: Google Maps). Measuring sites Rijeka-1 ( $45^{\circ} 19' 38.8''$  N,  $14^{\circ} 26' 47.9''$  E) and Rijeka-2 ( $45^{\circ} 19' 14.8''$  N,  $14^{\circ} 29' 0.5''$  E) are marked by numbers 1 and 2, while the two locations of the Rijeka Oil Refinery (ROR), Mlaka and Urinj, are indicated by the letters M and U, respectively. The lower panel shows a view of the ROR plant in Urinj from the northern part of the Island of Krk (photo by Berislav Rožman, 28 June 2009, at 16:42 LST).

Table 1: List of measured parameters and the percentage of available hourly means for the investigated period from 1 January 2006 to 31 July 2010.

	RIJEKA-1 (%)	RIJEKA-2 (%)
Nitrogen dioxide (NO <sub>2</sub> )	93.99	80.60
Carbon monoxide (CO)	96.96	93.20
Hydrogen sulfide (H <sub>2</sub> S)	53.82	–
Sulfur dioxide (SO <sub>2</sub> )	77.38	72.34
Ozone (O <sub>3</sub> )	–	90.53
Benzene (C <sub>6</sub> H <sub>6</sub> )	45.50	–
Particulate matter (PM <sub>10</sub> )	92.56	79.43
Surface temperature	92.37	90.40
Relative humidity	72.31	91.27
Surface wind	95.83	91.28

### 3. Data analysis and discussion of results

Table 2 presents the simple statistics for all the data collected during the investigated period of 4.5 years. The results illustrate that Rijeka-1 is more affected by traffic as compared to Rijeka-2, because it has higher average and maximum concentrations for both NO<sub>2</sub> and PM<sub>10</sub>. In contrast, higher average and maximum SO<sub>2</sub> concentrations at Rijeka-2 suggest that this site is more affected by the oil refinery as compared to Rijeka-1. All of the above are in accordance with the information regarding the purpose of these two sites as stated on the NAQN website.

According to Alebić-Juretić (2008), the ambient SO<sub>2</sub> concentrations recorded at several urban sites in 2000 varied roughly between 25 and 40 µg m<sup>-3</sup>, whereas current concentrations are smaller (14.1 and 21.6 µg m<sup>-3</sup> for Rijeka-1 and Rijeka-2, respectively). The mean NO<sub>2</sub> concentration at Rijeka-2 (16.6 µg m<sup>-3</sup>) is substantially less as compared to the values at the beginning of the year 2000 (approximately between 24 and 44 µg m<sup>-3</sup>). However, the decrease in concentration is not observed in the center of Rijeka (Rijeka-1, 28.9 µg m<sup>-3</sup>).

The summary results for meteorological data drew our attention for three reasons. First, at both sites, the minimum recorded temperature was exactly 0.0 °C, although according to the Meteorological and Hydrological Service of Croatia's (MHS) website ([http://meteo.hr/index\\_en.php](http://meteo.hr/index_en.php)), the daily mean temperature in Rijeka in January 2010 was below 0 °C over several consecutive days. Moreover, according to the Climate atlas of Croatia (Zaninović et al., 2008), temperatures as low as –11.4 °C have been recorded in Rijeka in the past (period 1961–2000). However, such low temperatures are in Rijeka rather rare. Second, the maximum relative humidity recorded at both sites was approximately 81 % and 82 %, respectively. Generally, higher maximum values



Table 2. Statistics for all data.

	Mean	St. dev.	Minimum	Maximum
RIJEKA-1				
NO <sub>2</sub> [ $\mu\text{g m}^{-3}$ ]	28.9	18.1	2.0	138.0
CO [ $\text{mg m}^{-3}$ ]	0.5	0.3	0.1	3.2
H <sub>2</sub> S [ $\mu\text{g m}^{-3}$ ]	1.2	0.7	0.5	19.4
SO <sub>2</sub> [ $\mu\text{g m}^{-3}$ ]	14.1	17.4	2.0	355.6
C <sub>6</sub> H <sub>6</sub> [ $\mu\text{g m}^{-3}$ ]	0.9	0.9	0.3	12.7
PM <sub>10</sub> [ $\mu\text{g m}^{-3}$ ]	24.7	15.5	5.0	291.2
Temperature [ $^{\circ}\text{C}$ ]	14.5	7.5	0.0	41.2
Rel. humidity [%]	57.8	15.8	12.3	81.7
Wind speed [ $\text{m s}^{-1}$ ]	0.6	0.3	0.0	3.6
RIJEKA-2				
NO <sub>2</sub> [ $\mu\text{g m}^{-3}$ ]	16.6	15.5	2.0	129.0
CO [ $\text{mg m}^{-3}$ ]	0.3	0.2	0.1	5.9
SO <sub>2</sub> [ $\mu\text{g m}^{-3}$ ]	21.6	32.3	2.0	492.1
PM <sub>10</sub> [ $\mu\text{g m}^{-3}$ ]	18.4	12.3	5.0	278.0
O <sub>3</sub> [ $\mu\text{g m}^{-3}$ ]	77.6	28.0	2	187.2
Temperature [ $^{\circ}\text{C}$ ]	15.5	7.5	0.0	39.3
Rel. humidity [%]	58.0	15.1	12.6	80.8
Wind speed [ $\text{m s}^{-1}$ ]	0.6	0.5	0.0	3.5

during precipitation events, are expected. It is well known that precipitation events are common for Rijeka – the average annual precipitation amount is between 1500 and 1750 mm (Zaninović et al., 2008). Additionally, according to the MHS climatological reports ([http://meteo.hr/index\\_en.php](http://meteo.hr/index_en.php)), the winter in 2008/2009 in Rijeka was wet, that is, the precipitation was greater than average; thus, for this period, larger maximum relative humidity values should have been recorded. Third, wind speeds at both the sites were  $0.6 \text{ m s}^{-1}$ , on average, which is low as compared to the average speeds recorded at 10 m above ground level at the meteorological measuring site maintained by the MHS. For example, during sea-land breeze conditions, measured speeds at the Rijeka MHS site are approximately  $1.5 \text{ m s}^{-1}$  on average (Prtenjak and Grisogono, 2007). Similarly, according to the modeled climatological values (Bajić et al., 2007), average wind speeds at 10 m above ground level over Rijeka should be approximately  $2\text{--}3 \text{ m s}^{-1}$ . The most likely reason for low wind speeds observed at the NAQN sites- Rijeka-1 and Rijeka-2 is the sheltered position of both measuring sites. Unfortunately, at the NAQN website, there is no information on the anemometers' heights. However, according to the MHS (Žibrat Z., personal communication, 2010), cup anemometers are placed at 10 m above the ground at

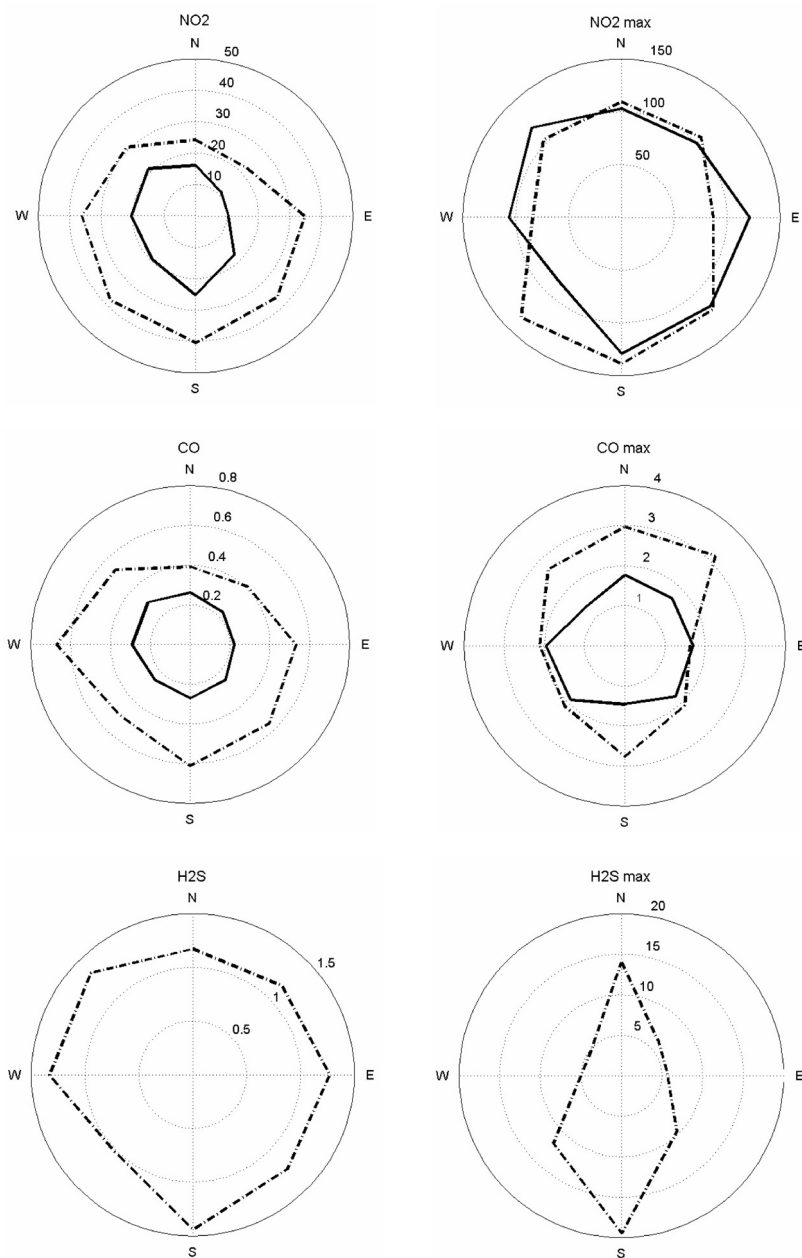
both the sites. Nonetheless, urban measuring sites that are designed to monitor the air quality do not need to satisfy the meteorological standards regarding the placement of instruments (such as prescribed minimum distance from the obstacles, height above the ground, flat grassy terrain, etc.), which are fulfilled by the meteorological measurement network; their main purpose is to record pollutant concentrations at selected localities rather than to collect meteorological data that are comparable with the data from the meteorological network.

Figure 2 shows the average pollutant concentrations at the two sites with respect to the observed wind directions (Table 3). Each wind direction was analyzed separately to account for the relative position of the measuring site with respect to different pollution sources. Once more, the data confirm the significance of the urban traffic for Rijeka-1 because it is well known that vehicular traffic is an important source of  $\text{NO}_x$ , CO and  $\text{PM}_{10}$  (e.g., Bešlić et al., 2005). We believe that the absence of  $\text{C}_6\text{H}_6$  in the northeastern flows most likely reflects the fact that greater than 50 % of the  $\text{C}_6\text{H}_6$  data were missing (Table 1). Furthermore, patterns of maximum concentrations at Rijeka-1 do not follow the patterns of average concentrations. Instead, they are almost always related to the most frequent southern ( $\text{NO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{SO}_2$ ) or northern (CO,  $\text{C}_6\text{H}_6$  and  $\text{PM}_{10}$ ) wind flows. Finally, average concentrations of  $\text{PM}_{10}$  are clearly stretched in the along-street (NE-SW) direction suggesting the line-shape of major emission sources of particles, that is, vehicular emissions combined with the resuspension of particles from the street surfaces.

Although mean  $\text{NO}_2$  concentrations at Rijeka-2 are substantially lower than those at Rijeka-1, the maximum concentrations for both the sites are comparable. The roses of the average and the maximum  $\text{SO}_2$  concentrations in both the sites do not explicitly suggest the transport of  $\text{SO}_2$  from the RNR plant in Urinj toward the measuring sites. We believe that this is due to the observed

Table 3. Total number of hours with specific wind direction ( $n$ ) and relative frequencies ( $f$ ) of individual wind directions.

Direction	RIJEKA-1		RIJEKA-2	
	$n$	$f$ (%)	$n$	$f$ (%)
N	17065	45.2	6233	17.3
NE	6574	17.4	7738	21.5
E	563	1.5	6612	18.4
SE	1614	4.3	3694	10.3
S	7194	19.1	4473	12.4
SW	2597	6.9	2087	5.8
W	243	0.6	1177	3.3
NW	1886	5.0	3946	11.0



**Figure 2.** Hourly mean (left) and hourly maximum (right) pollutant concentrations with respect to the wind direction. Apart from CO, which is given in  $\text{mg m}^{-3}$ , all other pollutant concentrations are measured in  $\mu\text{g m}^{-3}$ . Rijeka-1 and Rijeka-2 data are shown with dot-dashed and full line, respectively.



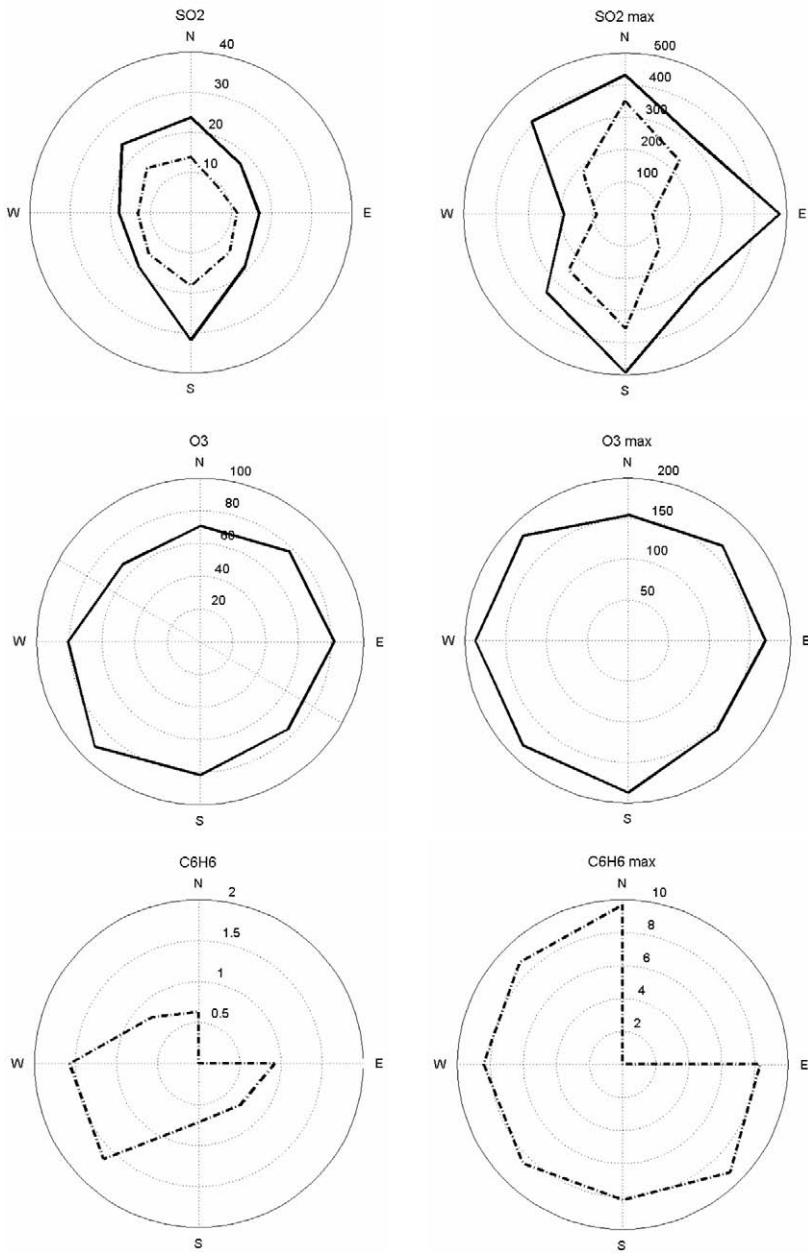
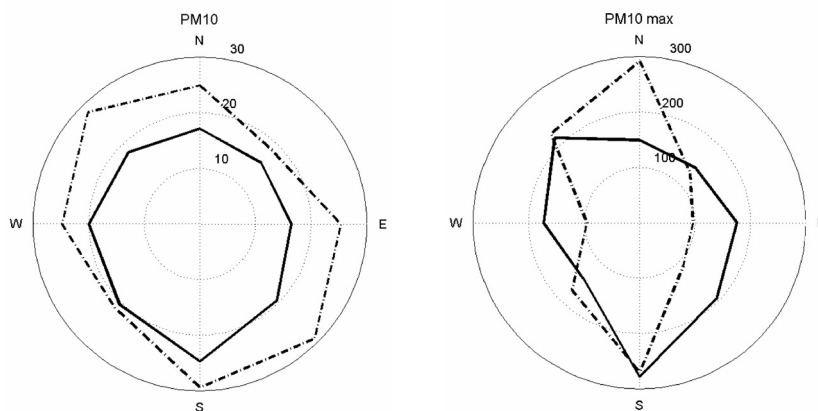


Figure 2. Continued.



**Figure 2.** Continued.

winds at the two sites being strongly affected by nearby obstacles. Thus, they represent purely local airflow conditions. In other words, locally observed wind directions do not reflect the transport of pollutants to distances of several kilometers. However, this transport is suggested by the fact that the  $\text{SO}_2$  concentrations at the site closer to the oil refinery (Rijeka-2) are, on average, approximately 50 % higher than the concentrations at the more distant site (Rijeka-1). Unfortunately, the concentrations of other pollutants emitted by the oil refinery ( $\text{H}_2\text{S}$  and  $\text{C}_6\text{H}_6$ ), which may further corroborate the above mentioned hypothesis, are not measured at both the sites. The highest  $\text{O}_3$  concentrations are related to the southwestern flows, although the differences between individual wind directions are not very distinct. This finding illustrates that the possible advection of  $\text{O}_3$  and/or its precursors is dominated by the local photochemical production of  $\text{O}_3$ .

Figures 3–5 show the average diurnal, annual and weekly courses of the observed parameters. Despite our previously expressed doubts regarding observed values of meteorological parameters (particularly, minimums of temperature and maximums of relative humidity), Figures 3 and 4 show reasonable patterns of wind speed, relative humidity and air temperature. For example, the diurnal variations in the wind speed exhibit similar shapes as the one in Prtenjak and Grisogono (2007), except for smaller wind speeds and smaller amplitudes. Furthermore, the relative humidity at both the sites decreases with an increase in the temperature and vice versa, at both the diurnal and the annual scales. We conclude that the average temporal variations of temperature were negligibly contaminated by errors introduced by improper measurements of relatively rare temperatures below  $0^\circ\text{C}$ .

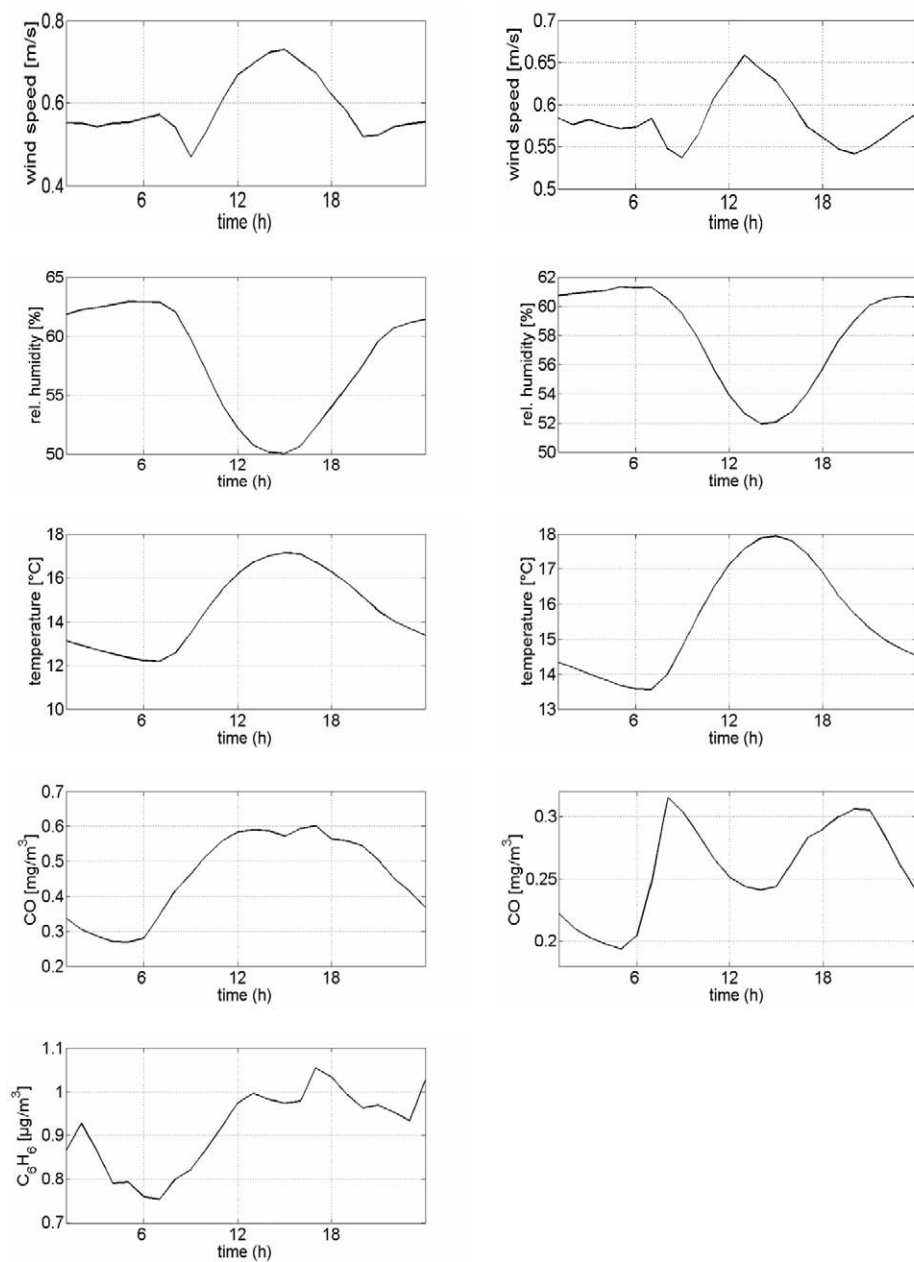
Generally, pollutant concentrations depend on both emission levels and atmospheric conditions (e.g., Bešlić et al., 2007). Thus, the effects of periodic

variations in meteorological conditions and human activity are also seen in the diurnal and annual variations in pollutant concentrations. In contrast, the weekly variations in pollutant concentrations should solely reflect the effects of anthropogenic emissions.

Apart from  $O_3$ , pollutant concentrations at both the sites begin to increase in the early morning hours, between 5 and 7 AM local standard time (LST) (Fig. 3). Furthermore, the elevated concentrations of CO and  $NO_2$  at Rijeka-1 which are substantially higher than the concentrations of the same pollutants at Rijeka-2, are stretched over a long time interval (~10 h), indicating dense vehicular traffic throughout the day. In contrast, the two separated maximums at Rijeka-2 clearly suggest morning and evening rush hours. The dissimilar behavior of  $O_3$  with a minimum value in the morning (at 9 AM LST) and an inverse diurnal variation as compared to CO and  $NO_2$ , illustrates the well known destruction of  $O_3$  by vehicular exhaust fumes (e.g. Alebić-Juretić, 2007). However, the high nocturnal  $O_3$  peak with the value comparable with the daytime maximum is not fully understood and needs further investigation.

Despite being affected by the simultaneous effects of emissions, meteorological influence can be illustrated by an example of the wind speed. Under same emission conditions, higher wind speeds cause more efficient ventilation eventually resulting in lower pollutant concentrations. Conversely, weaker winds result in higher concentrations. For example, the highest wind speeds at both the sites occurred in the early afternoon hours (Figure 3) around 15 and 13 LST for Rijeka-1 and Rijeka-2, respectively. The figure shows that the wind maximums at Rijeka-1 coincided with a slight decrease in pollutant concentration, i.e., afternoon secondary minimum found at 15 LST for all pollutants except  $SO_2$ . At Rijeka-2, the secondary afternoon minimum is found for CO and  $NO_2$ , but with a time lag of one hour. Similar effects on the annual scale (Fig. 4) could be seen for Rijeka-1 (wind maximum in July accompanied with  $C_6H_6$  minimum) and Rijeka-2 (wind maximum in December accompanied with  $NO_2$  and  $PM_{10}$  minimums).

At the annual scale (Fig. 4), apart from  $O_3$  and  $PM_{10}$  at Rijeka-2, maximum pollutant concentrations are found in the winter months. These can be attributed to higher anthropogenic emissions (heating, denser traffic during the colder months of the year and industrial activities, which are more intense as compared to the summer months). Thus, the effects of ventilation due to stronger wintertime winds are dominated by increased emissions. The July maximum of  $O_3$  reflects a photochemical production of ozone due to higher solar radiation. Although the solar radiation data were not available, we found that the ozone maximum coincides with the maximum temperature and the minimum relative humidity, both suggesting low cloudiness, that is, higher incoming radiation. Considering that maximum  $PM_{10}$  concentrations were recorded at Rijeka-2 for the month of June, we found that maximum  $PM_{10}$  concentrations coincide with the minimum wind speed at the same site, i.e. with the weak ventilation at the measuring site. Minimum concentrations of CO and  $NO_2$  at both the sites,



**Figure 3.** Diurnal variations of measured parameters for Rijeka-1 (left) and Rijeka-2 (right) with respect to the local standard time.

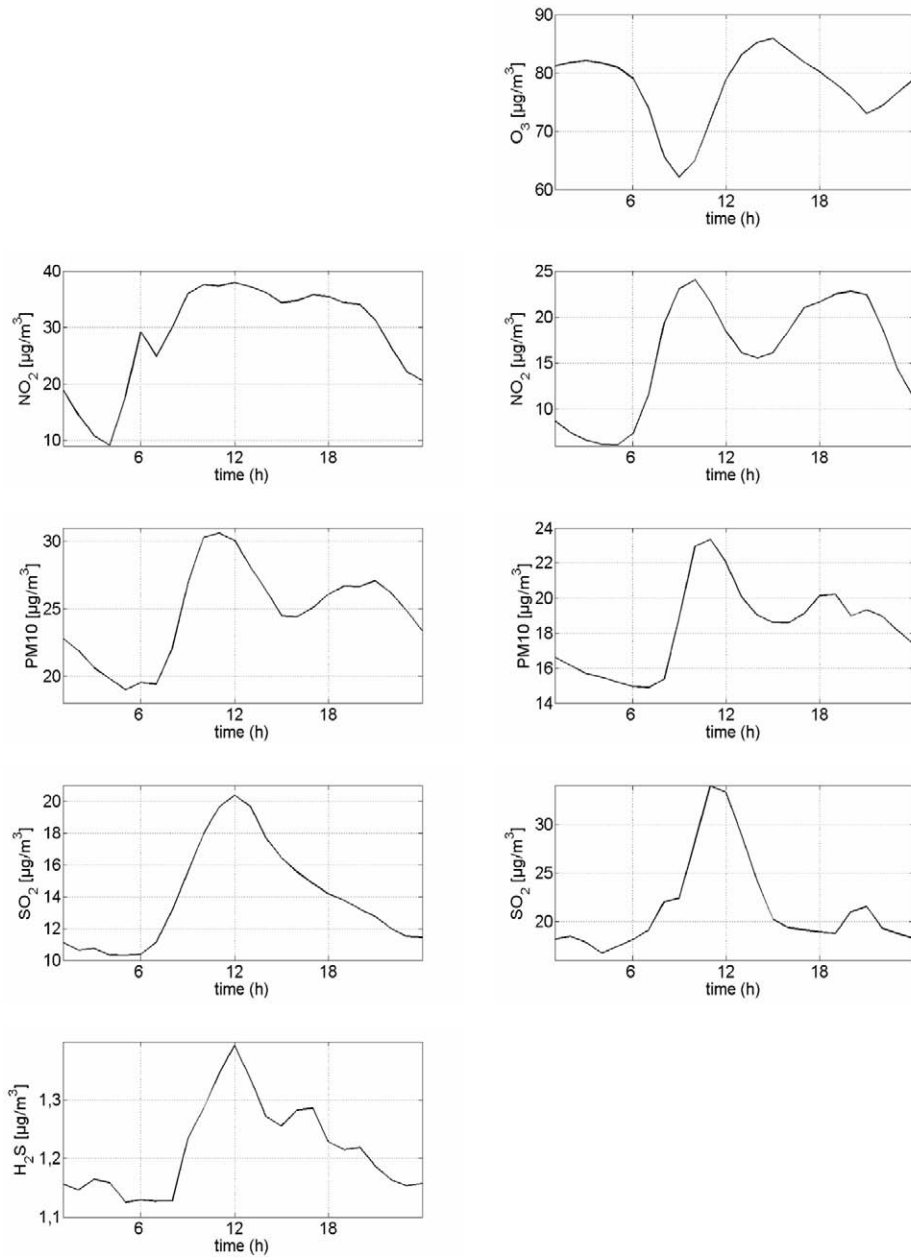
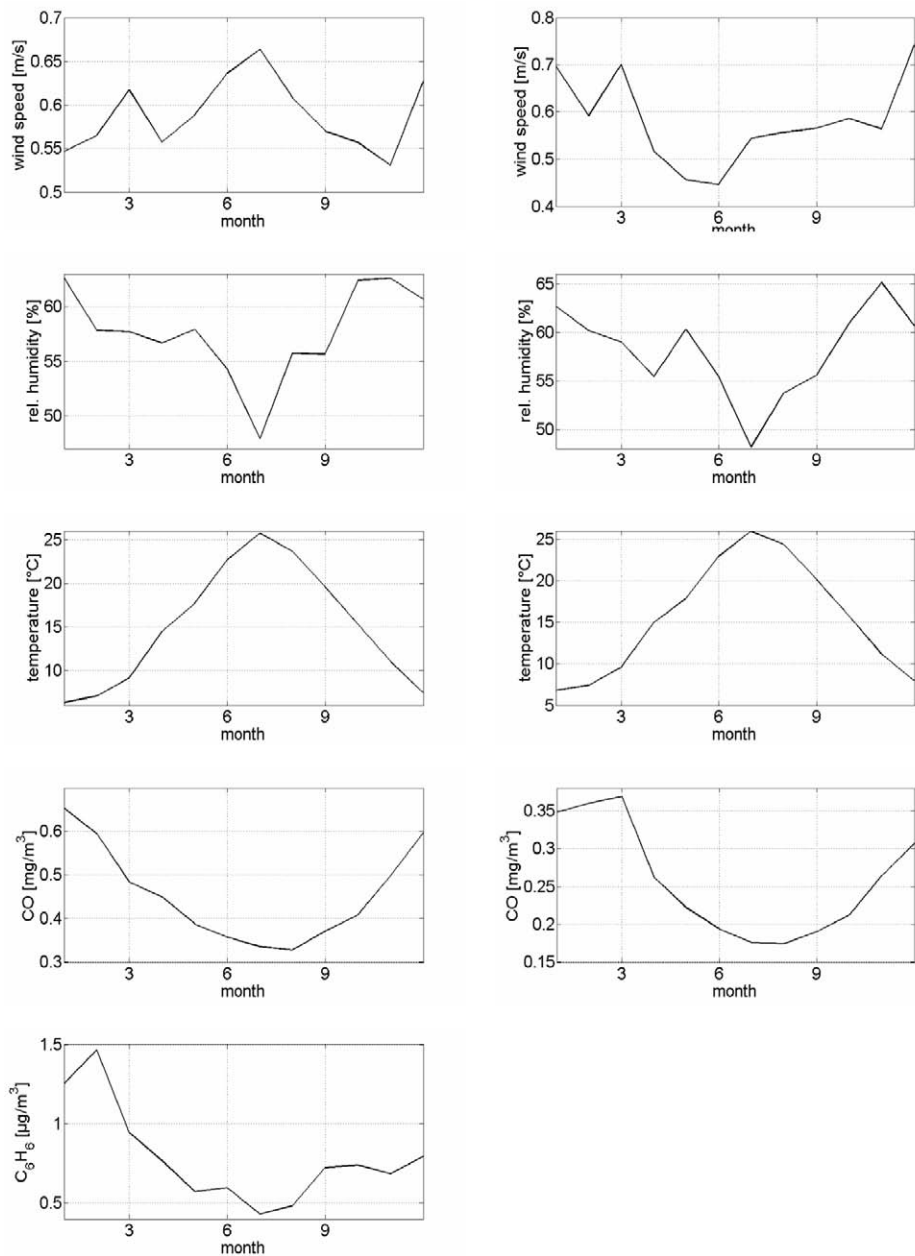


Figure 3. Continued.



**Figure 4.** Annual variations of measured parameters for Rijeka-1 (left) and Rijeka-2 (right).



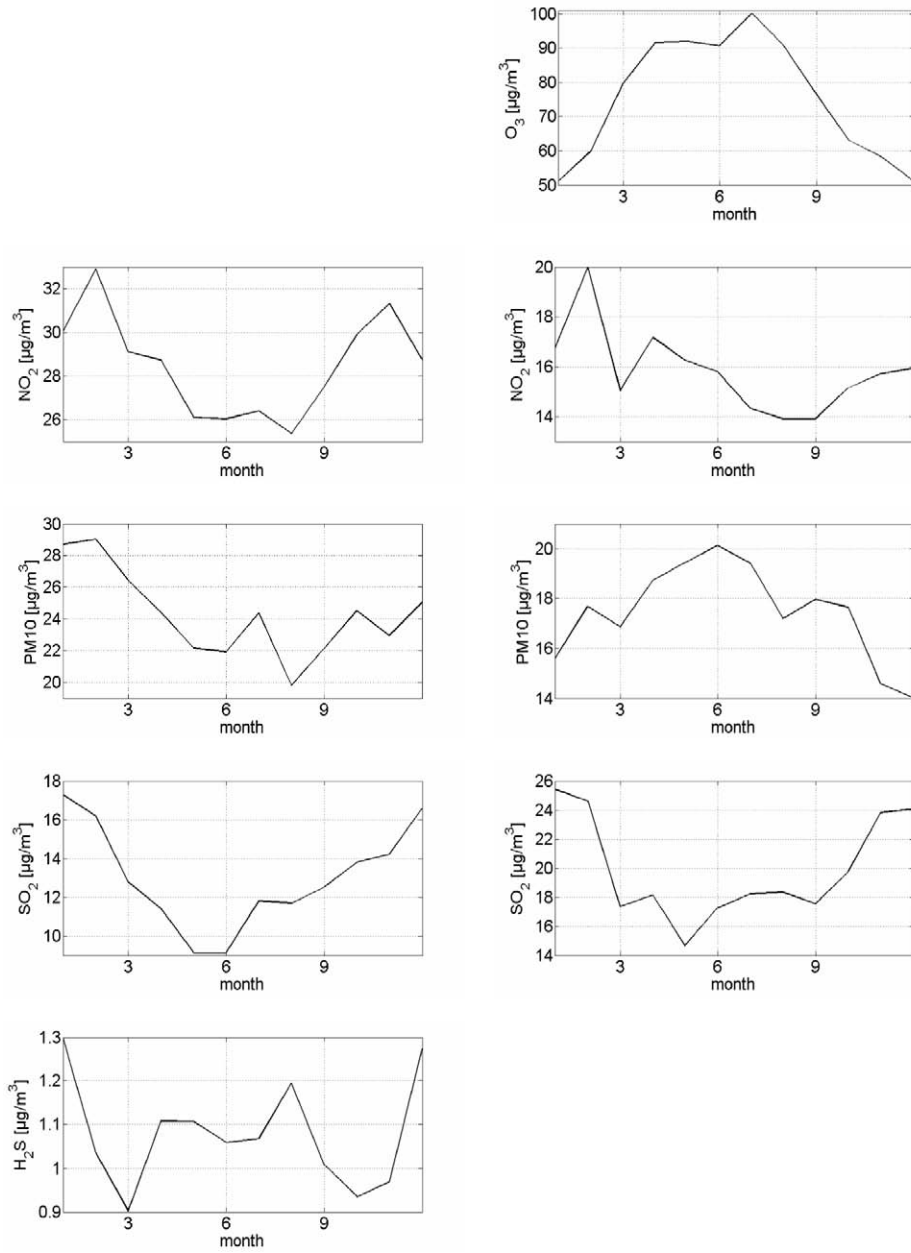
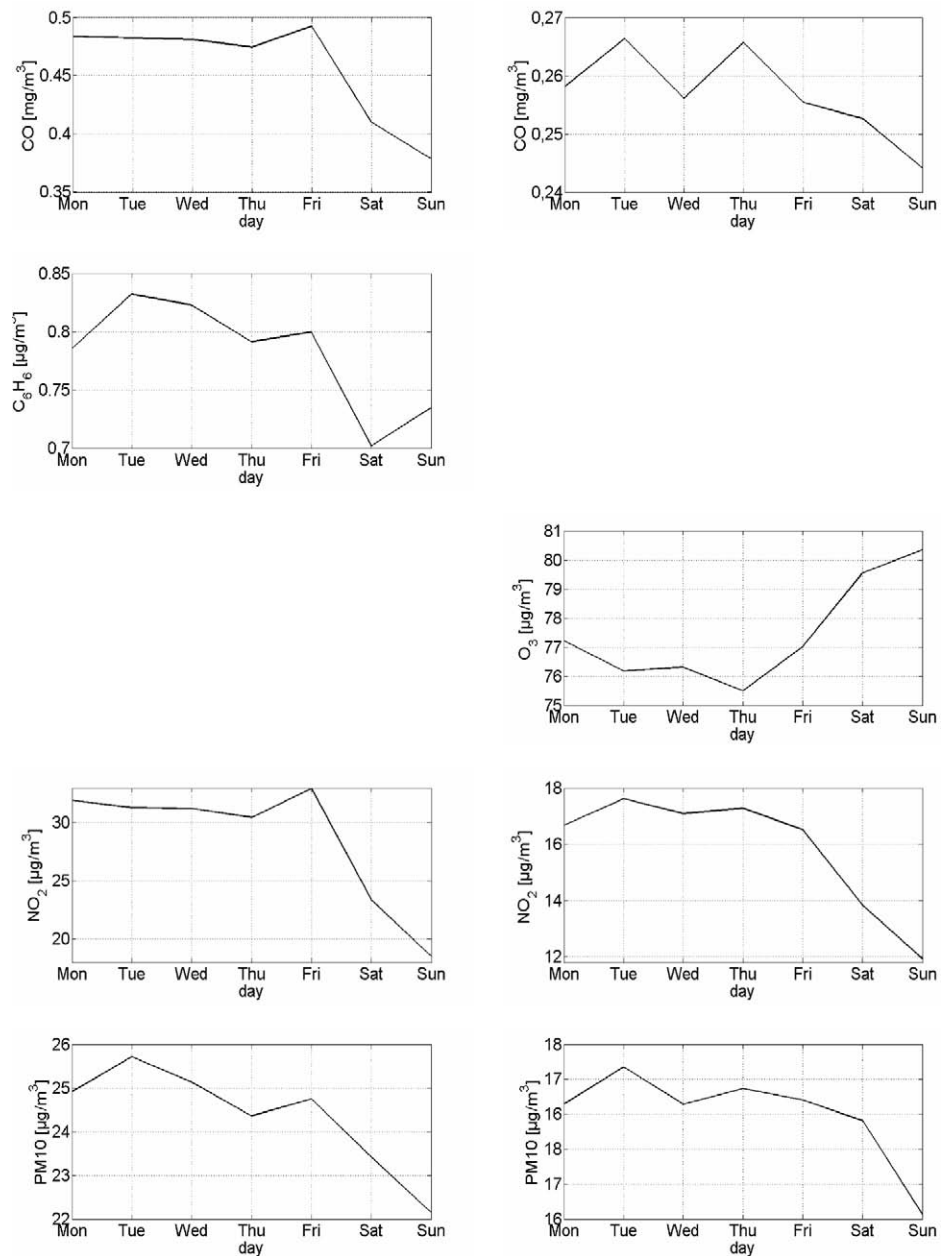
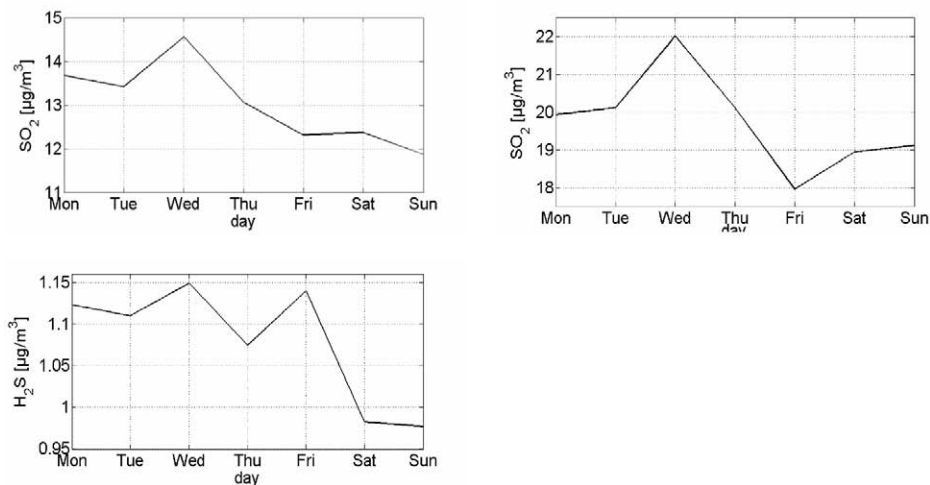


Figure 4. Continued.



**Figure 5:** Weekly variations of measured parameters for Rijeka-1 (left) and Rijeka-2 (right).



**Figure 5.** Continued.

and  $\text{C}_6\text{H}_6$  and  $\text{PM}_{10}$  at Rijeka-1 are due to the low anthropogenic emissions found in July and August, while minimum concentration of  $\text{O}_3$  in January is due to the weak photochemical production. In contrast, the December minimum of  $\text{PM}_{10}$  at Rijeka-2 coincides with the wind speed maximum at the same site. However, we do not have an explanation for the May-June minimum of  $\text{SO}_2$  concentrations at both the sites as well as the March minimum of  $\text{H}_2\text{S}$ .

The weekly variations of pollutant concentrations for all pollutants except  $\text{O}_3$  and  $\text{SO}_2$  at Rijeka-2, show noticeably lower concentrations during the weekend as compared to the week days. The Sunday  $\text{O}_3$  maximum coincides with the  $\text{NO}_2$  minimum, that is, with less intense ozone destruction due to smaller emissions of vehicular exhaust fumes. It is interesting to note that the minimum of  $\text{SO}_2$  concentration occurs in Rijeka-2 on a Friday, perhaps caused by some specific dynamics of the production cycle in the ROR and/or other plants in the industrial zone of Rijeka, emitting  $\text{SO}_2$ . However, we do not have information on the details of the industrial activities to further discuss this phenomenon.

#### 4. Summary and conclusions

The study investigated the pollutant concentrations of  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{PM}_{10}$  measured at the hourly time scale at the two urban sites in Rijeka over the past 4.5 years (1 January 2006–31 July 2010). The sites are maintained by the National Air Quality Network (NAQN) of Croatia. According to the NAQN, the purpose of Rijeka-1, located in the center of the town, is

the continuous monitoring of the pollution levels caused mainly by the vehicular traffic. Rijeka-2 is in the southeastern part of the town closer to the industrial zone and the oil refinery and is designed to monitor the pollution levels in the residential and the industrial parts of Rijeka. The observed concentration data together with the data for the wind speed, temperature and relative humidity are available at the NAQN website (<http://zrak.mzopu.hr/>).

Although the diurnal and the annual variations of available meteorological data appear reasonable and agree with the results of the other studies, we believe that the lowest temperatures and the highest relative humidity at both the sites are not recorded accurately based on the information on the meteorological conditions for the town of Rijeka by other sources (climate atlas, MHS data). It is interesting to note that at both the sites, the lowest recorded hourly mean temperatures were exactly 0.0 °C and that exactly equal, and unusually high minimum values were recorded at three other urban sites maintained by the NAQN (i.e., three sites in Zagreb during 1 October 2008–30 September 2009; for more details, see Strahovnik, 2010).

The pollutant concentrations of emissions emitted mainly by the vehicular traffic were substantially higher at the center of the town as compared to the site closer to the industrial zone. The NO<sub>2</sub>, CO and PM<sub>10</sub> concentrations at Rijeka-1 were on an average, 74 %, 67 % and 34 %, higher, respectively, than at Rijeka-2. In contrast, SO<sub>2</sub> concentration which is mainly a by-product of the oil refinery was on an average, 53 % higher at Rijeka-2 as compared to Rijeka-1. The findings confirm that the locations of the two sites are in accordance with their main purposes. Additionally, the difference in the exposure to the traffic emissions is also evident in the diurnal variations of the pollutant concentrations at the two sites. Whereas elevated concentrations of NO<sub>2</sub> and CO at Rijeka-1 are found through a long time period of approximately 10 hours, indicating a uniformly dense traffic in the center of the town during the daytime, at Rijeka-2, two separate peaks corresponding to the morning and evening rush hours are observed.

Both the mean and the maximum hourly mean pollutant concentrations of SO<sub>2</sub>, H<sub>2</sub>S and C<sub>6</sub>H<sub>6</sub> calculated for each wind direction do not explicitly suggest the pollution transport from the oil refinery towards the measuring sites due to the wind directions recorded at the measuring sites representing purely local airflow conditions dominated by nearby obstacles. Therefore, they are unable to capture the effects of pollution advection over distances of several kilometers or more. In order to assess the contributions of advection from the industrial area, the airflow data representative of the larger scale (e.g. Bešlić et al., 2008; Prtenjak et al., 2009) should be employed. Nevertheless, substantially higher SO<sub>2</sub> concentrations at the site closer to the refinery as compared to the more distant Rijeka-1 confirm the importance of advection.

The diurnal and the annual variations in pollutant concentrations at both the sites reflect the combined effects of anthropogenic emissions and meteorological conditions. However, based on the data available, we can explain nei-

ther the May-June minimum of SO<sub>2</sub> concentrations at both the sites, nor the March minimum of H<sub>2</sub>S at Rijeka-1. Also, it is unclear why the nocturnal O<sub>3</sub> concentrations are high. The weekly variations of all the pollutants generally reflect the human activities. The only surprising finding is the Friday minimum of SO<sub>2</sub> at Rijeka-2.

Finally, the average SO<sub>2</sub> concentrations over the last 4.5 years at the two urban sites are approximately two times less than the SO<sub>2</sub> concentrations measured at several urban sites ten years ago (Alebić-Juretić, 2008). A substantial decrease in NO<sub>2</sub> concentrations was also found for the residential/industrial site Rijeka-2, whereas at the traffic affected Rijeka-1, the concentration is within the range of the concentrations reported for the early 2000s.

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## References

- Alebić-Juretić, A. (1995): Trends in sulphur dioxide concentrations and sulphur deposition in the urban atmosphere of Rijeka (Croatia), *Water Air Soil Pollut.*, **85**, 2199–2204.
- Alebić-Juretić, A., Cvitaš, T., Kezele, N., Klasinc, L., Pehcec, G. and Šorgo, G. (2007): Atmospheric particulate matter and ozone under heat-wave conditions: do they cause an increase of mortality in Croatia?, *B. Environ. Contam. Tox.*, **79**, 468–471, doi: 10.1007/s00128-007-9235-2.
- Alebić-Juretić, A. (2008): Airborne ammonia and ammonium within the Northern Adriatic area, Croatia, *Environ. Pollut.*, **154**, 439–447.
- Bajić, A., Ivatek-Šahdan, S. and Horvath, K. (2007): Spatial distribution of wind speed in Croatia obtained using the ALADIN model, *Croat. Met. J.*, **42**, 67–77.
- Bešlić, I., Šega, K., Šišović, A. and Klaić, Z. B. (2005): PM<sub>10</sub>, CO and NO<sub>x</sub> concentrations in the Tuhobić road tunnel, Croatia, *Int. J. Environ. Pollut.*, **25**, 251–262.
- Bešlić, I., Šega, K., Čačković, M., Klaić, Z. B. and Vučetić, V. (2007): Influence of weather types on concentrations of metallic components in airborne PM<sub>10</sub> in Zagreb, Croatia, *Geofizika*, **24**, 93–107.
- Bešlić, I., Šega, K., Čačković, M., Klaić, Z. B. and Bajić, A. (2008): Relationship between 4-day air mass back trajectories and metallic components in PM<sub>10</sub> and PM<sub>2.5</sub> particle fractions in Zagreb air, Croatia, *B. Environ. Contam. Tox.*, **80**, 270–273, doi: 10.1007/s00128-008-9360-6.
- Cukrov, N., Francišković-Bilinski, S., Hlača, B. and Barišić, D. (2010): A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia, *Mar. Pollut. Bull.* (in press), doi: 10.1016/j.marpolbul.2010.08.020.
- Čanić, K. Š., Vidić, S. and Klaić, Z. B. (2009): Precipitation chemistry in Croatia during the period 1981–2006, *J. Environ. Monit.*, **11**, 839–851, doi: 10.1039/b816432k.
- Forgić, I. (2010): Studija kvalitete zraka na području Rafinerije nafte Rijeka. Završni rad. Sveučilište u Zagrebu, Centar za poslijediplomske studije, Sveučilišni interdisciplinarni poslijediplomski studij Ekoinženjerstvo, Zagreb, 57 pp.
- Kampa, M. and Castanas, E. (2008): Human health effects of air pollution, *Environ. Pollut.*, **151**, 362–367.
- Klaić, Z. B., Belušić, D., Grubišić, V., Gabela, L. and Čoso, L. (2003): Mesoscale airflow structure over the northern Croatian coast during MAP IOP 15 – a major bora event, *Geofizika*, **20**, 23–61.

- Klaić, Z. B., Pasarić, Z. and Tudor, M. (2009): On the interplay between sea-land breezes and Etesian winds over the Adriatic, *J. Marine Syst.*, **78** (Suppl. 1), S101–S118, doi: 10.1016/j.jmarsys.2009.01.016.
- Mohorović, L. (2004): First two months of pregnancy – critical time for preterm delivery and low birthweight caused by adverse effects of coal combustion toxics, *Early Hum. Dev.*, **80**, 115–123.
- Monks, P. S., Granier, C., Fuzzi, S., Stohl, A., Williams, M. L., Akimoto, H., Amann, M., Baklanov, A., Baltensperger, U., Bey, I., Blake, N., Blake, R. S., Carslaw, K., Cooper, O. R., Dentener, F., Fowler, D., Fragkou, E., Frost, G. J., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hansson, H. C., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I. S. A., Jenkin, M. E., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M. G., Lee, J. D., Liousse, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Moussiopoulos, N., Orlando, J. J., O'Dowd, C. D., Palmer, P. I., Parrish, D. D., Petzold, A., Platt, U., Pöschl, U., Prevot, A. S. H., Reeves, C. E., Reimann, S., Rudich, Y., Sellegri, K., Steinbrecher, R., Simpson, D., ten Brink, H., Theloke, J., van der Werf, G. R., Vautard, R., Vestreng, V., Vlachokostas, C. and von Glasow, R. (2009): Atmospheric composition change – global and regional air quality, *Atmos. Environ.*, **43**, 5268–5350, doi: 10.1016/j.atmosenv.2009.08.021.
- Mücke, H.-G. (2008): Air quality management in the WHO European Region – Results of a quality assurance and control programme on air quality monitoring (1994–2004), *Environ. Int.*, **34**, 648–653, doi:10.1016/j.envint.2007.12.008.
- Nitis, T., Kitsiou, D., Klaić, Z. B., Prtenjak, M. T. and Moussiopoulos, N. (2005): The effects of basic flow and topography on the development of the sea breeze over a complex coastal environment, *Q. J. Roy. Meteor. Soc.*, **131**, 305–327.
- Prtenjak, M. T. and Grisogono, B. (2007): Sea-land breeze climatological characteristics along the northern Croatian Adriatic coast, *Theor. Appl. Climatol.*, **90**, 201–215, doi: 10.1007/s00704-006-0286-9.
- Prtenjak, M. T., Jeričević, A., Kraljević, L., Bulić, I. H., Nitis, T. and Klaić, Z. B. (2009): Exploring atmospheric boundary layer characteristics in a severe SO<sub>2</sub> episode in the north-eastern Adriatic, *Atmos. Chem. Phys.*, **9**, 4467–4483.
- Strahovnik, T. (2010): Koncentracije lebdećih čestica PM<sub>10</sub> u ovisnosti o prometu i meteorološkim elementima. Završni rad. Sveučilište u Zagrebu, Centar za poslijediplomske studije, Sveučilišni interdisciplinarni poslijediplomski studij Ekoinženjerstvo, Zagreb, 43 pp.
- Zaninović, K., Gajić-Čapka, M., Perčec Tadić, M. et al. (2008): *Climate atlas of Croatia 1961–1990, 1971–2000*, Meteorological and Hydrological Service of Croatia, Zagreb, 200 pp.
- Žabkar, R., Rakovec, J. and Gaberšek, S. (2008): A trajectory analysis of summertime ozone pollution in Slovenia, *Geofizika*, **25**, 179–202.

## SAŽETAK

### Kakvoća zraka u Rijeci

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Analizirane su srednje satne koncentracije dušičnog dioksida (NO<sub>2</sub>), ugljičnog monoksida (CO), sumporovodika (H<sub>2</sub>S), sumpornog dioksida (SO<sub>2</sub>), ozona (O<sub>3</sub>), benzena (C<sub>6</sub>H<sub>6</sub>) i lebdećih čestica (PM<sub>10</sub>) izmjerene tijekom posljednje 4,5 godine na dva urbana mjerna mjesta u Rijeci. Jedno mjesto je u središtu grada, dok je drugo u njegovom jugoistočnom dijelu te je bliže industrijskoj zoni Rijeke. Mjesto u središtu Rijeke pod velikim je utjecajem prometa te stoga ima bitno veće koncentracije NO<sub>2</sub>, CO i PM<sub>10</sub>, dok su na drugom mjernom mjestu koncentracije SO<sub>2</sub> puno veće. Dnevni i godišnji ho-



dovi koncentracija polutanata odražavaju dva utjecaja, ljudsku aktivnost i periodičke varijacije meteoroloških uvjeta, dok su prosječne tjedne varijacije u skladu s antropogenim emisijama. Konačno, trend opadanja koncentracija, koji je započeo sredinom osamdesetih godina prošlog stoljeća, i dalje je vidljiv u koncentracijama  $\text{SO}_2$  na oba mjerna mjesta te u koncentracijama  $\text{NO}_2$  na mjernom mjestu koje je bliže riječkoj industrijskoj zoni.

*Ključne riječi:* koncentracije, urbano onečišćenje, promet, rafinerija nafte, hodovi

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