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An Analysis of the Pollution Problem in Slavonski Brod (Eastern Croatia)

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A B S T R A C T

H_2S, $PM_{2.5}$, O_3, NO_2, SO_2 and meteorological parameters such as temperature, relative humidity, precipitation, wind speed and wind direction were measured simultaneously in an eastern Croatian town called Slavonski Brod during the season winter/spring 2010. Emissions from the nearby cross-border (Bosnia and Herzegovina) oil refinery were identified as sources of temporary elevated concentrations of H_2S. The maximum daily averages of $PM_{2.5}$ concentrations during the winter period were as high as 240 μg m^{-3} which is a value 10 times greater than the threshold prescribed by the World Health Organization. It is considered that the heating season, dense traffic, intense industrial activities and temperature inversion during stable weather conditions are prevailing contributors to higher winter concentrations of $PM_{2.5}$. The results of the principal component analysis technique (PCA) have shown that lower air temperature, lower wind speed and higher relative humidity play a significant role in the winter pollution episodes. From a public health point of view, implementation of measures aimed at reducing the levels of H_2S and $PM_{2.5}$ should be considered.

Key words: *air quality, principal component analysis, human health, eastern Croatia*

Introduction

Air pollution episodes are defined as the events in which levels of pollutants exceed the respective national thresholds to a great extent. The main generators of pollutants are: industrial processes, burning fossil fuels and vehicular traffic[1]. The by-products of these operations (particulate matter (PM), H_2S, CO, NO_x, SO_2, volatile organic compounds (VOCs)) have been emitted in the environment in enormous amounts, seriously threatening human health and the biosphere. The major source of fine particulate matter ($PM_{2.5}$, diameter ≤2.5μm) comes from human activity such as fuel combustion, industrial processes, re-suspension and non-industrial fugitive sources (roadway dust, agricultural wind erosion, etc).

Due to their small size, $PM_{2.5}$ particles have relatively long atmospheric residence times (in the order of days), so they can be carried far away from their origin. Therefore, pollutants emitted somewhere in Europe can affect concentrations of $PM_{2.5}$ not only in neighbouring countries but also in very distant places[2]. Unlike coarse particulate matter (PM_{10}, diameter ≤10 μm) which contains mainly crustal materials (Fe, Ca and Si), fine particles are composed mainly of sulphates, other secondary material, many toxic elements such as As, Se, Cd and Ni, and polynuclear aromatic compounds. Since $PM_{2.5}$ particles are tiny, they have high alveolar penetration capacity, thereby triggering a local inflammatory process with circulatory repercussion[3].

Recent studies of the link between exposure to $PM_{2.5}$ and increased mortality have revealed that the most endangered populations are children, older patients and patients with chronic diseases[3,4].

The World Health Organization (WHO)[2] guideline values for 24-hour mean values of $PM_{2.5}$ amount to 25 μg m^{-3}.

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Anthropogenic releases of H_2S into the air result from industrial processes, but the gas is also present at sewage treatment plants, tanneries, coke oven plants, farms with manure storage and landfills. Oil and gas operations may emit H_2S regularly or by accident during the extraction, storage or processing stage. Hydrogen sulfide ambient air concentrations from natural sources are estimated[5] to range from 0.154 to 0.462 $\mu g\ m^{-3}$. Human exposure to exogenous hydrogen sulfide refers mostly to inhalation and the gas is rapidly absorbed into the lungs. The effects of exposure to H_2S as an irritant and asphyxiant on human health depend largely on the concentration and length of exposure. Lower doses of H_2S and related gases appear to be innocuous, but the effects of prolonged exposure are associated with headaches, nasal symptoms and respiratory diseases[5,6]. This is particularly evident if the fact that the atmospheric residence time of H_2S may be as high as 42 days in winter is taken into consideration[5]. The ability to detect the odour of H_2S varies amongst individuals, though the best estimates of the odour threshold for H_2S range from 7 to 10 $\mu g\ m^{-3}$. The Croatian 1-hour average and 24-hour average threshold of 7 $\mu g\ m^{-3}$ and 5 $\mu g\ m^{-3}$ respectively must not be exceeded more than seven times in a year[7].

Ozone is a secondary pollutant produced through a complex series of reactions between primary pollutants, mainly oxides of nitrogen, sulfur oxides, carbon oxides, VOCs (volatile organic compounds) and sunlight. High concentrations of O_3 are associated with an increased risk of asthma; it can intensify airway inflammation and also potentiate the airway response to the inhaled allergens[2]. Emissions of NO and NO_2 originate from anthropogenic sources, the main contributors of which are traffic and stationary combustion. Paradoxically, O_3 concentrations in the air might increase if the emission of nitrogen oxides (NO_x) goes down. In terms of gases, the solubility governs which proportion may be absorbed in the upper airway and which proportion will reach the terminal air sacs of the lungs. Unlike SO_2 which is rather soluble and consequently absorbed early in the airway, leading to airway resistance and mucous secretion, NO_2 and O_3 are relatively insoluble and thus able to penetrate deep into the lungs and the air sacs causing pulmonary edema. Most of the studies associate levels of NO_2 and SO_2 to the levels of particulate matter and O_3 in the air, hence the damaging effects are evaluated for all of the four pollutants together[1,2].

The potential air pollution sources in Slavonski Brod include a nearby oil refinery located across the border with Bosnia and Herzegovina, the Đuro Đaković industry and vehicle emissions from surrounding roads featured by dense traffic.

There are no available studies about pollution issues with respect to this part of Croatia, so it is very important to explore experimental data coming from this region in order to get a comprehensive monitoring picture of the entire area. For the purpose of assessment of the state of ambient air in the Slavonski Brod area, the data of simultaneous measurements of $PM_{2.5}$, H_2S, O_3, NO_2, SO_2, and meteorological parameters were analysed and the results thereof are now presented in this paper.

Multivariate data analysis (MDA) techniques like principal component analysis (PCA) have been proved to be an effective tool to investigate the relationship between voluminous data such as air pollution and meteorological records. Recent studies have shown that the PCA method is successfully applied to identify the dominant multivariate relationships presented by such complex data[8]. The goal of this study is to assess the exposure of inhabitants of the Slavonski Brod area to different pollutants (namely $PM_{2.5}$, H_2S, O_3, NO_2 and SO_2.) Also, the aim of conducting this research is to identify, by means of PCA, the hidden relationships between air pollutants and meteorological variables.

Measurements and Methods

Our monitoring site, the town of Slavonski Brod with its population of about 63,000, belongs to one of the biggest urban and industrial centre in the eastern Croatia.

The monitoring station is lifted 20 m above the ground and located in the western outskirts of Slavonski Brod at 45.6° N, and 17.59° E, close to the Sava River and in the zone of influence of the refinery located in the neighbouring country of Bosnia and Herzegovina. The city is surrounded by the mountain range of Dilj in the north and the Sava River in the south. The annual average temperature is 11°C (spring: 11°C, summer: 21°C, autumn: 11.8°C, winter: 0.2°C).

The measuring site in Slavonski Brod is a part of the national network for continuous air quality monitoring

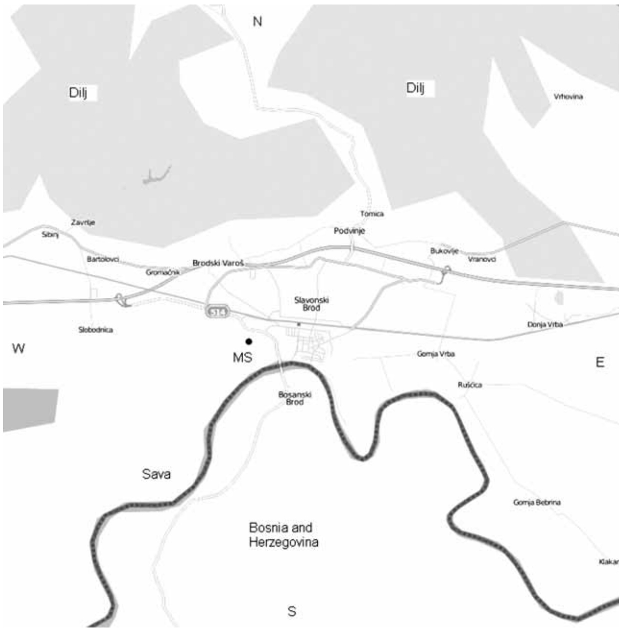

Fig. 1. Map of Slavonski Brod area with the position of the measurement site (MS) (source: Google Maps).

established by the Croatian Ministry of Environmental Protection, Physical Planning and Construction. The network is engaged with surveillance of concentration of NO_2, H_2S, SO_2, $PM_{2.5}$ and O_3, temperature (T, °C), relative humidity (RH, %), wind speed (WS, m/s), wind direction (WD, degrees) and precipitation (Pr/mm). The figures representing concentrations of NO_2, H_2S, SO_2, $PM_{2.5}$ and O_3 are expressed in $\mu g\ m^{-3}$. The measurement period involved the time span from January 10th to May 11th, 2010.

PCA models were applied in order to investigate relationships of meteorological variables and pollutant concentrations[8]. In the present study statistical analysis were performed using the statistical software Statistica, version 7.0.

Results

Average hourly distributions

Figures 2–6 show the average hourly variations of all the measured primary and secondary pollutants obtained from January 19th through May 11th 2010 in the form of »box and whiskers« plots. As shown in Figure 2, most of the maximum hourly values of H_2S concentrations were higher than the hourly standards ($7 \mu g\ m^3$) stipulated by the national ambient air quality in Croatia[7]. Elevated concentrations of $PM_{2.5}$ are also very prominent (Figure 3). Their maximum hourly concentrations reached 300 $\mu g\ m^{-3}$. Nevertheless, the maximum hourly concentrations of SO_2, NO_2 and O_3, did not exceed the threshold of 350, 200 and 120 $\mu g\ m^{-3}$, respectively (Figures 4–6). A comparison of the average diurnal pollutants profiles show that the two concentration peaks of NO_2 are located in the front and at the back the peak for O_3. Obviously, higher SO_2 concentrations appear during later morning hours or around noon, which is a tendency similar to that of H_2S.

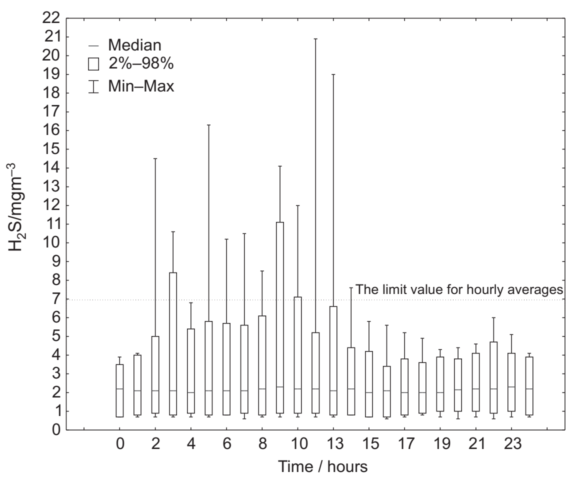

Fig. 2. Diurnal distribution of H_2S concentrations in Slavonski Brod in the season winter/spring 2010.

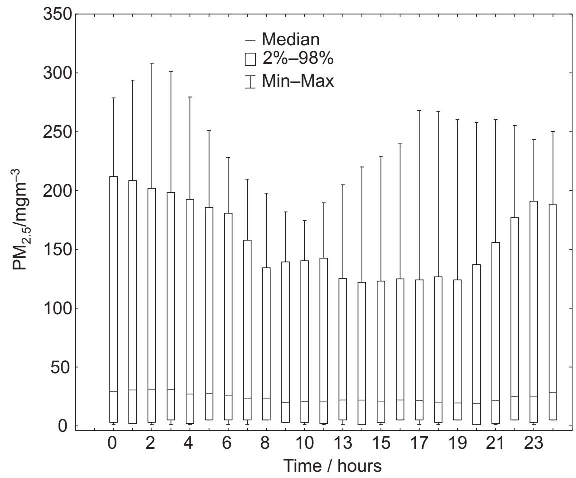

Fig. 3. Diurnal distribution of $PM_{2.5}$ concentrations in Slavonski Brod in the season winter/ spring 2010.

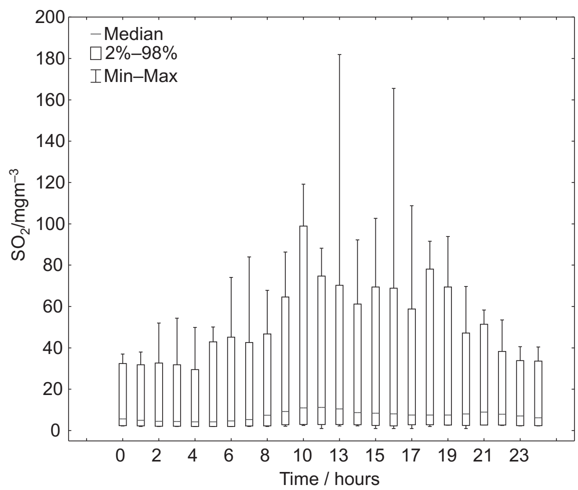

Fig. 4. Diurnal distribution of SO_2 concentrations in Slavonski Brod in in the season winter/ spring 2010.

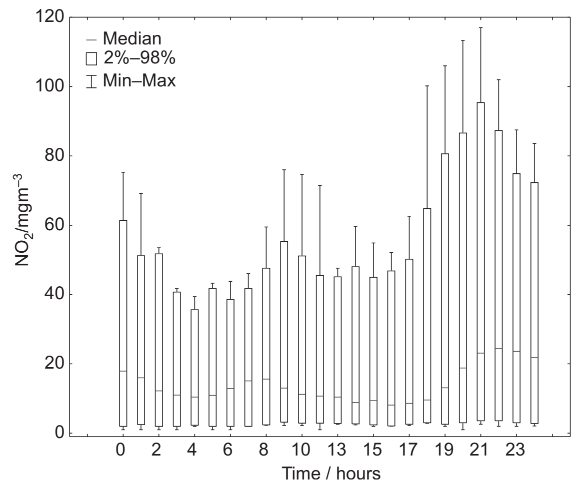

Fig. 5. Diurnal distribution of NO_2 concentrations in Slavonski Brod in in the season winter/ spring 2010.

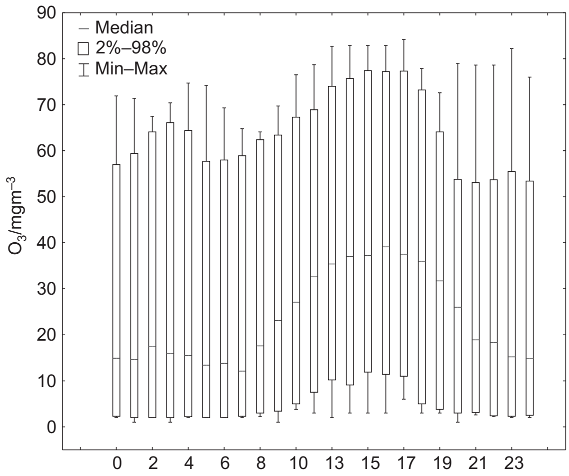

Fig. 6. Diurnal distribution of O_3 concentrations in Slavonski Brod in in the season winter/ spring 2010.

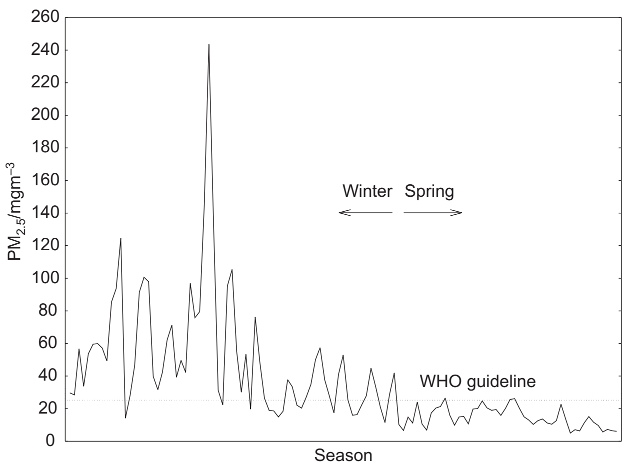

Fig. 8. Average diurnal changes of $PM_{2.5}$.

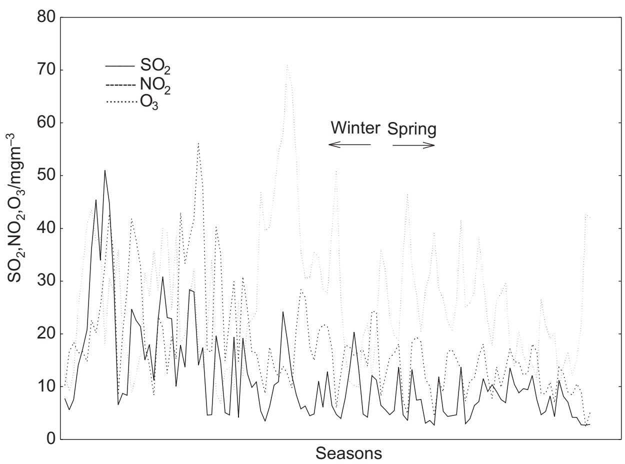

Fig. 9. Average diurnal changes of SO_2, NO_2 and O_3.

Daily averages of $PM_{2,5}$, H_2S, NO_2, SO_2 and O_3 concentrations

The WHO guideline for 24-h $PM_{2.5}$ value totals 25 μg m^{-3}. This value was exceeded on 58 (app. 50%) occasions in the area of Slavonski Brod in the target period. Regarding the 24-h limit value of 5 μg m^{-3} for H_2S, this measurement site recorded only one reading beyond the limit.

As seen in Figures 7–9 and unlike for H_2S, the daily average of SO_2, NO_2 and $PM_{2.5}$ concentrations decreased at the end of the winter period. The NO_2, SO_2 and O_3 concentrations stayed within the thresholds and therefore they are shown together in Figure 9.

Wind roses

The technique of rose plotting was applied in order to understand behaviour and origin of all pollutants. Figure 10 presents the correlations between the wind and pollutant concentrations. The correlations between the concentrations of H_2S and SO_2, and wind direction clearly show that higher values have something in common with southwest (180°–270°) air masses. On the contrary, the density of points shows that higher concentrations of O_3, NO_2 and $PM_{2.5}$ are mostly situated in the sector extending from east (or both from east and from west) of the monitoring station. Different diurnal variations of H_2S and SO_2 as well as different wind roses regards remaining pollutants indicate that one might have to search for their origin somewhere else.

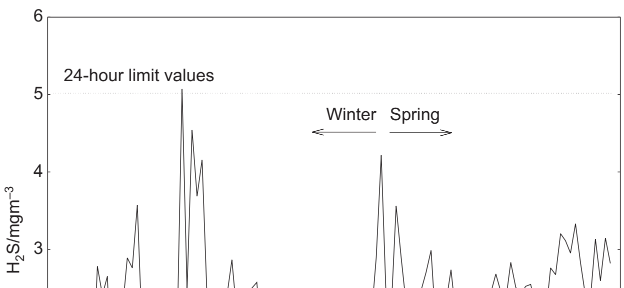

Fig. 7. Average diurnal variations of H_2S.

Principal component analysis

Interpretation of the results of PCA is based on visualization of the component scores and loadings. In general:

$$PC_i = l_{1i}X_1 + l_{2i}X_2 + \ldots + l_{ni}X_n (1)$$

where PC*i* is the *i*-th principal component and l_{ji} is the loading of the observed variable *Xj*.

The principal component loadings can be plotted for any pair of principal components (PCs). In order to avoid misclassifications arising from different orders of the magnitude of measured variables, the data were mean

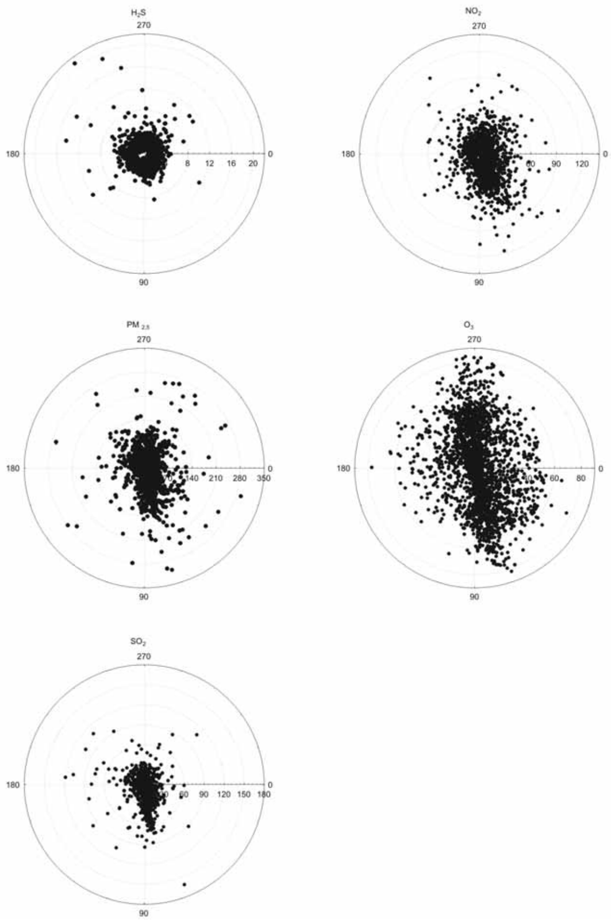

Fig. 10. Measured pollutant concentrations at measured wind directions-wind roses.

(average) centred and divided by relevant standard deviations. PCA on the basis of the correlation matrix of the data provide the results given in Figure 11 (loadings and scores). Firstly, grouping of the objects (samples) can be recognized and secondly, the importance of different elements for discrimination between the clusters can be discussed. Four main clusters of samples can be distinguished: a rather compact cluster (I) in the left portion of Figure 11 (which contains most of the samples). It therefore defines the most common condition, i.e. determines situations of higher frequency. Since the variables that point toward certain objects are more important for those objects, it is obvious that these days were drier with calm winds and lower H_2S, SO_2, NO_2 and $PM_{2.5}$ concentrations. While the days in the upper right portion of Figure 11 (Cluster II-winter period) display periods with windy, colder and more humid days as well as with the highest concentrations of SO_2, NO_2 and $PM_{2.5}$, cluster III (also winter period) contains days that are characterized by higher H_2S levels. Consequently, these two clusters represent somewhat less frequent cases, although with higher concentrations of pollutants. Cluster IV (spring period) is characterized with warmer and windy weather, lower relative humidity and higher O_3 concentrations.

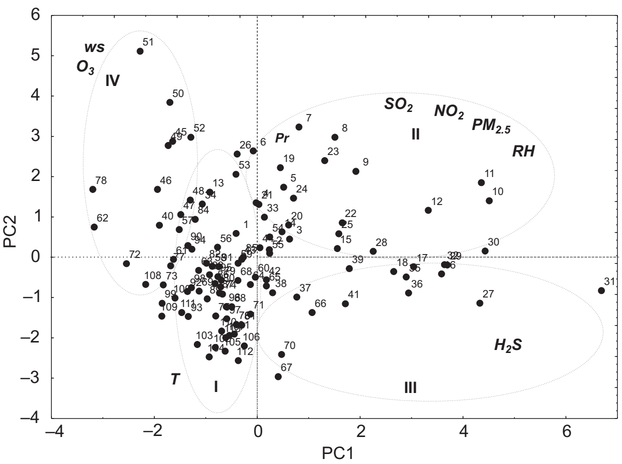

Fig. 11. Scores and loadings plot in the PC space (PC1/PC2).

Discussion

Qualitative assessment of the impact of anthropogenic sources of all the measured pollutants can be obtained by examination of the diurnal variability of pollutants concentrations and the extent to which it follows human activity patterns. As indicated, it came to frequent non-adherence to the WHO[2] (for $PM_{2.5}$) and Croatian standards[7] (for H_2S) during the two observed seasons. In January and February, $PM_{2.5}$ concentrations were high and fell at the end of winter as shown in Figure 8. It is apparent that the traffic-related sources were not among those which are to be predominantly blamed for the variability of $PM_{2.5}$ concentrations. Various factors, and not only emissions of the vehicles or plants, may contribute to the $PM_{2.5}$ deviations. Seasonal differences of $PM_{2.5}$ may be explained by higher emission during winter season (fossil fuel combustion from industrial activities and largely domestic heating). In addition, due to the slow movement of lower air masses, these meteorological conditions encourage accumulation of $PM_{2.5}$ in a stable volume of air. The combination of these factors may result in accumulation of $PM_{2.5}$ in the ambient air, leading to its frequent violations. Particulate matter from various sources follows the appertaining short-term (daily, monthly) and seasonal trends (annually). Space heating during colder seasons generate a larger amount of combustion-related PM emissions during the day. The combination of the above factors can result in accumulation of $PM_{2.5}$ in the air and bring to frequent violations of the new WHO standard. Exposure to higher concentrations of $PM_{2.5}$ is associated with increased risk of circulatory-cause mortality[3] and hospital admissions[9]. It is important to emphasize that the daily mean concentrations of $PM_{2.5}$ in Madrid[3,4] and Italy[10] were significantly lower (maximum value of only 71 $\mu g/m^3$ and 131 μgm^{-3} respectively) than those measured in the Slavonski Brod area during the same season.

The major anthropogenic source of NO_2 in urban areas is fossil fuel combustion from motor vehicles. The distribution of NO_2 is generally characterized by a bimodal phenomenon and thus the similarity between NO_2 and traffic cycles (two peaks corresponding to rush hours; in the morning between 6 and 8 a.m. and in the afternoon between 4 and 6 p.m.) suggests that in this area, NO_2 levels are related to the traffic flow. Regarding the influence of wind direction, the maximum NO_2 concentrations were bound to the north-east wind, so the correlation between the slightly higher observed values of NO_2 concentrations and the north-easterly winds can be attributed to the town centre as the source of this kind of pollution. This corroborates our assumption that the main source of NO_2 in the Slavonski Brod area is urban car and bus traffic. The diurnal variations of O_3 during the winter season were similar to those determined in this part of Croatia in the spring and summer cycles[8]. The sudden increase of O_3 concentrations at the beginning of March can be explained by a simultaneous temperature and sunshine duration jump. Ozone is the only gaseous pollutant, concentration of which inversely correlates with remaining pollutants (Figure 11). This happens quite often in urban areas where the diurnal cycle of ozone is influenced by traffic. The inverse correlation between NO_2 and O_3 reaffirms the so-called »titration effect« of NO on O_3. The positive correlation between O_3 and wind speed implies that ozone is probably transported from the surrounding rural regions situated at the eastern and western edges of the town.

The distinct morning and evening go-to-work peaks in the case of H_2S, $PM_{2.5}$ and SO_2 are not obvious, so different diurnal variations and wind roses of $PM_{2.5}$, H_2S and SO_2 confirm that there are other sources of those pollutants. Furthermore, higher H_2S, NO_2, $PM_{2.5}$ and NO_2 (Figure 11) concentrations were registered at lower wind speeds which indicates the dilution of these air pollutants by wind as well as the fact that they were all produced in the vicinity of the measurement site. This finding could be conditioned by the distance between measurement site and the source of pollutants: with a shorter distance, the wind acts as a dilution factor, thus the majority of pollutants seem to originate from the town and the immediate vicinity of the town. As shown in Figure 10, the correlation between the concentrations of H_2S and SO_2 and the wind direction clearly shows that higher concentrations are associated with south-westerly winds (180°–270°). This side correspons to the refinery's area located on the right bank of the Sava River. Although the Croatian H_2S 1-hour average of 7 $\mu g\ m^{-3}$ should not be exceeded more than seven times in a year, this standard was exceeded 22 times during the observation period. The results of this study show that during winter season, levels of $PM_{2.5}$ in the Slavonski Brod area rise and there might be significant health implications associated with these high concentrations.

Since the respiratory tract is the major target organ of H_2S and $PM_{2.5}$ toxicity, humans with asthma, elderly people and young children with compromised respiratory function represent sensitive populations[3,4,9]. Many of the processes producing particulate matter also produce other gaseous pollutants, so the negative impact of all the pollutants on human health should not be underestimated. Knowing pollutant concentrations is very important in the fields such as ecology and medicine. Accurate investigation of these concentrations and of the appertaining influence of meteorological factors could help pollinosis, asthmatic and cardiovascular patients.

Conclusion

The reported data on O_3, $PM_{2.5}$, H_2S, SO_2 and NO_2 concentrations constitute the first comprehensive study of atmospheric pollutants in the town of Slavonski Brod. Somewhat higher concentrations of H_2S and SO_2 are associated with lower wind speeds and south-westerly air mass movements, which indicates that these gasses are generated locally, i.e. in the vicinity of the measurement site. A respective comparison with the World Health Organization thresholds acknowledges the presence of the fine particle ($PM_{2.5}$) pollution issue in the Slavonski Brod area. Principal component analysis has turned out to be an effective method for investigating correlations between air pollutants and meteorological variables.

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ANALIZA PROBLEMA ZAGAĐENJA U SLAVONSKOM BRODU (ISTOČNA HRVATSKA)

S A Ž E T A K

H_2S, $PM_{2.5}$, O_3, NO_2, SO_2 i meteorološki parametri temperatura, relativna vlaga, padaline, brzina i smjer vjetra mjereni su istovremeno tijekom zime i proljeća 2010. u Slavonskom Brodu (istočni dio Hrvatske). Emisije obližnje rafinerije smještene u susjednoj državi Bosni i Hercegovini identificirane su kao izvori povremeno povišenih koncentracija H_2S. Maksimalne prosječne dnevne koncentracije $PM_{2.5}$ čestica tjekom zimskog perioda dostizale su čak 240 $\mu g\ m^{-3}$ što su vrijednosti 10 puta veće od graničnih vrijednosti propisanih od strane svjetske zdravstvene organizacije. Zaključeno je da su sezona grijanja, gušći saobraćaj, intenzivnija industrija i temperaturna inverzija tjekom stagnatnih vremenskih uvjeta odgovorni za povišene zimske koncentracije $PM_{2,5}$. Rezultati analize glavnih komponenata pokazali su da su epizode zimskog zagađenja povezane s nižom temperaturom, manjim brzinama vjetra i većom relativnom vlagom. S obzirom na ljudsko zdravlje neophodna je provedba mjera koje bi bile usmjerena na smanjenje koncentracija H_2S i $PM_{2.5}$.