



Air pollution levels near crossroads with different traffic density and the estimation of health risk

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Abstract The aim of this study was to determine the influence of traffic density on air pollutant levels as well as to analyse the spatial and temporal distribution of particulate pollutants and their health risk. The following species related to traffic pollution were measured: PM₁₀, elemental and organic carbon and polycyclic aromatic hydrocarbons (PAHs) in PM₁₀ and gas pollutants (SO₂, NO₂ and CO). The measurements were carried out at four crossroad sites in the city. Samples of PM₁₀ were collected over three

periods (6 am to 2 pm, 2 pm to 10 pm and 10 pm to 6 am) on working days and weekends. Statistically significant differences were found between sampling sites for all pollutant concentrations, except for NO₂. The highest mass concentrations of PM₁₀, carbon and PAHs were observed in the south of the city with the highest traffic density. Concentrations of gasses (CO and NO₂) showed high values in morning and in the late afternoon and evening (west and east). At all measuring sites, the highest concentration of particle-bound pollutants was mostly recorded during morning and afternoon, except at the south, where elevated PAHs concentrations were recorded during night period, which indicated that residential heating takes up a portion of pollution sources in this area. Although for most of the pollutants the concentrations varied

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during the day, statistically significant differences between sampling periods were not found. The highest health risk was obtained at the south, where it was scored as significant.

Keywords EC · Gas pollutants · OC · PAH · Urban traffic

Introduction

Air pollution has a large influence on ecosystems and the quality of life (Cavalli et al., 2016; Monks et al., 2009; Putaud et al., 2010; Van Dingenen et al., 2004). Epidemiological studies have demonstrated that air pollution can cause adverse health effects such as cardiovascular, cardiopulmonary, incidence of dementia, and/or early mortality human exposure (Bernstein et al., 2004; Brunekreef & Holgate, 2002; Burnett et al., 2014; Calderón-Garcidueñas et al., 2020; Davidson et al., 2005; Donaldson et al., 2005; Fuzzi et al., 2015; Grahame et al., 2014; Lewtas, 2007; Pateraki et al., 2019; Perez et al., 2013; Pöhlker et al., 2017; Pöschl, 2005; Wang et al., 2017). The most important role in air pollution is attributed to concentrations of particulate matter with aerodynamic diameters smaller than 10 μm or 2.5 μm (PM₁₀, PM_{2.5}, respectively). PM is categorized by different chemically multifaceted mixtures of organic and inorganic components. However, to determine the exposure to all specific components has not been possible so far. Instead, only some pollutants are measured to determine air quality, such as gas pollutants (sulphur dioxide, nitrogen monoxide and dioxide and carbon monoxide) and mass concentrations of the PM₁₀ or PM_{2.5} particle fraction. Recent studies have included measurements of elemental (EC) and organic (OC) carbon and polycyclic aromatic hydrocarbons (PAHs) in particulate matter, but almost exclusively in daily samples, while diurnal variations of organic content have not been analysed (Cavalli et al., 2016; Godec et al., 2016; Jakovljević et al., 2015). Many natural and anthropogenic sources (car exhausts, biomass burning and domestic heating) emit EC, PAHs and gas pollutants into the atmosphere, and they are often used as indicators for traffic emission (Alves et al., 2016; Bernalte et al., 2012; Finardi et al., 2017; Gaga & Ari, 2018; Hanedar et al., 2014; Hassan, 2018;

Karanasiou et al., 2015; Kosztowniak et al., 2015; Pio et al., 2011; Samara et al., 2014). The source of organic carbon, which is a combination of organic composites such as aliphatic and aromatic hydrocarbons, can be primary (emitted directly in particulate phase) or secondary (from gas-to-particle conversions in the atmosphere). Polycyclic aromatic hydrocarbons (PAHs) in air occur as a compound mixture. Congeners with two or more aromatic rings exist in the vapour phase, while four and more aromatic rings PAHs are adsorbed on particulate matter (Alves et al., 2016; Bernalte et al., 2012; Finardi et al., 2017; Gaga & Ari, 2018; Hanedar et al., 2014; Masiol et al., 2012; Mastral, 2003). PAHs were the primary pollutants recognized as potential carcinogens. Previous studies have shown that carcinogenicity and toxicity were associated with PAH bounden to airborne rather than with PAH existing in vapour phases (Cautreels & Van Cawenberghe, 1978; Lyall et al., 1988). Kuo, Chien, et al. (2012) found significant correlations between concentrations of PAH and PM particles, and PAHs have been the most studied organic compound for exploring mutagenic and carcinogenic activity (Amarillo et al., 2014). Exposures to PAHs include breathing indoor and ambient air and/or ingestion of contaminated food. Long-term exposure to PAHs can cause toxic effects such as breathing problems, lung function abnormalities, decreased immune function, kidney and liver damage, skin irritation and inflammation. Some studies suggest correlations between elevated blood pressure and higher risk of cardiovascular events with exposure to PAHs (Yin et al., 2018).

Apart from particulate air pollution, gaseous pollutants can also affect the environment, human health and quality of life (Balaceanu & Iorga, 2010; Bernstein et al., 2004; Gibson et al., 2013; Iorga, 2016). Some of these gas pollutants such as nitrogen monoxide and dioxide and carbon monoxide are in the city mostly traffic-related (Oliveri Conti et al., 2017).

Traffic-related studies in Europe are mostly carried out in large cities in countries with developed economies (Cazier et al., 2016; Finardi et al., 2017; Manoli et al., 2016). Investigations of the influence of traffic pollutants on human health are relatively rare in newer EU member states or non-EU states (Jelić & Klaić, 2010; Perez et al., 2013; Stankovic et al., 2012). However, the situation in such countries may differ greatly due to different topography and conditions,

such as types of fuels (gas or diesel) and age of vehicles. For example, the average age of cars in Europe is 11.6 years, but it varies from 9 years in Germany, Austria or Switzerland to 14–16 years in, for example, Hungary or Romania (<https://www.acea.be/statistics/article/average-vehicle-age>). In Croatia, the average age of vehicles is 12.6, with more than 60% cars older than 10 years, which is lower than the European average (<https://www.cvh.hr/en/home/>). Zagreb, the Capital of Croatia, is surrounded on the north by the Medvednica Mountain, while on the south it is open and stretches across the Sava River. In the eastern and western parts, Medvednica also extends, but it is not as closed as on the northern side. For that reason, survey measurements should be carried out in different parts of the city and in different parts of the week and days (weekdays, weekends, mornings, afternoons and overnight).

The aim of this study was to:

- Determine mass concentrations of gas pollutants (sulphur dioxide, nitrogen monoxide and dioxide and carbon monoxide) and particulate pollutants: PM₁₀, carbon species and polycyclic aromatic hydrocarbons (PAHs) in PM₁₀ and their spatial distribution in traffic loaded areas.
- analyse temporal variations of pollutants, especially particle-bounded organic compounds during the day and week.
- analyse the relationship between traffic density and the level of air pollution.
- determine the human health risk by using the ILCR formula with parameters from the literature to identify human exposure via inhalation.

Capsule

Results will provide a better insight into the carcinogenic potential of specific traffic related compounds and may be useful to comprehend the contribution of inhalable organic compounds to cancer risk as well as improved decisions on reducing traffic emissions and enhancing urban air quality.

Materials and methods

Sampling sites

Croatia is located in southern Central Europe and the northern Mediterranean. In the north, it borders with Slovenia and Hungary, on the east with Serbia and Bosnia and Herzegovina, on the south with Montenegro, and in the west with Italy by sea. Its land area is 56,578 km², and the surface of the coastal sea is 31,067 km². The Croatian Capital is Zagreb, and it is also the largest city in Croatia with 790,000 inhabitants (Census 2011). The city of Zagreb together with its neighbouring area encompasses more than a million people. Zagreb is positioned on the banks of the Sava River and on the hills of Medvednica mountain. It has a suitable geographical place among the Alpine, Dinaric, Adriatic and Pannonian areas due to the fact located on the route between central and southeastern Europe and the Adriatic Sea. The microclimate in Zagreb is moderate continental. The summers are hot and dry with average temperatures of 20 °C, while the winter is cold with average temperatures of 1 °C. During our period of measurements, the average temperature, pressure, relative humidity and precipitation were 10.3 °C, 1003.3 hPa, 84.2% and 7.1 l m⁻², respectively.

Traffic site 1 (TS1) was situated in the western part of Zagreb near cargo terminals, (N 45° 47' 57" E 15° 52' 49"). At this location, the three-week measurement period lasted from 29 September until 19 October 2014. The main sources of pollution at this site, except for traffic, stemmed from the nearby industry. Around TS1 during the measuring period, 76,017 vehicles were registered per day, of which 86% were personal vehicles (64,958 cars), 6% heavy cargo vehicles (over 3.5 tones, 4661 vehicles) and about 8% delivery vehicles under 3.5 tones (6398 vehicles). During morning rush-hour, from 7 to 8 am, 9107 vehicles were registered around TS1 and about 55% of them in the direction east–west on the main avenue.

Traffic site 2 (TS2) was situated in the eastern part of Zagreb, also near cargo terminals, (N 45° 48' 01" E 16° 03' 24"). At this location, the four-week measurement period lasted from 20 October until 16 November 2014. The main sources of pollution at this site, following traffic, originated from the nearby industry and house heating. Around TS2 during the measuring period and throughout the whole day, 74,466 vehicles

were registered, 62% of which were personal vehicles (46,070 cars), 30% heavy cargo vehicles (over 3.5 tones, 22,399 vehicles) and less than 10% delivery vehicles under 3.5 tones (5997 vehicles). During morning rush-hour, 4077 vehicles were registered around TS2 and about 81% of them in the direction east–west on the main avenue.

Traffic site 3 (TS3) was located in the centre of town near the main bus station (N 45° 48' 18" E 15° 59' 37"). At this location, the three-week measurement period lasted from 17 November to 7 December 2014. The main sources of pollution at this site, except for traffic, came from residential heating. Around TS3 during the measuring period and the entire day, 132,077 vehicles were registered, 90% were personal vehicles (122,813 cars), less than 2% heavy cargo vehicles (over 3.5 tones, 2275 vehicles) and 5% delivery vehicles under 3.5 tones (6989 vehicles). During morning rush-hour, from 7 to 8 am, 8719 vehicles were registered around TS3 and about 50% of them in the direction east–west on the main avenue.

Traffic site 4 (TS4) was located in the southern part of Zagreb near the largest roundabout in the city and one of the exits from Zagreb, (N 45° 46' 41" E 15° 57' 18"). At this location, three-week measurement period lasted from 8 to 21 December 2014. The main sources of pollution at this site, excluding traffic, stemmed from residential heating. Around TS4 during the measuring period, and during the whole day, 206,056 vehicles were registered, of which 86% were personal vehicles (177,440 cars), less than 5% heavy cargo vehicles (over 3.5 tones, 9667 vehicles) and less than 10% delivery vehicles under 3.5 tones (18,949 vehicles). During morning rush hour, 21,065 vehicles were registered around TS3 and less than 60% of them in the direction east–west. Figure 1 shows the locations of all of the traffic sites around the city.

The data for traffic density for all sampling stations were provided by the Integrated Traffic of Zagreb Area Company. The number of vehicles is shown in Fig. 2.

PM₁₀ mass concentrations

Samples of PM₁₀ were collected on working days and weekends at three different periods of the day (6 am to 2 pm, 2 pm to 10 pm and 10 pm to 6 am) during three or four week period in the autumn and winter of 2014. Samples were collected on quartz fibre filters

previously pre-fired at 900 °C for three hours. The mass concentration of particulate matter was determined gravimetrically according to the EN 12341:2014 norm. Before and after sampling, filters were conditioned at a constant temperature (20 ± 1 °C) and relative air humidity (45–50% RH) for 48 h, prior to the first weighing and reweighing after the next 24 h.

Carbon analyses

The thermal-optical transmittance method (TOT) was used for determining the content of organic, elemental and total carbon (TC, a sum of EC and OC) in the PM₁₀ fraction by using a Carbon Aerosol Analyzer (Sunset Laboratory Inc.) with a flame ionization detector (FID), (Birch & Cary, 1996; Godec et al., 2012, 2016; Karanasiou et al., 2015) following a NIOSH-like protocol called Quartz according to technical report CEN/TR 16,243:2011. A portion of each sample (1.5 cm²) was used for OC and EC analyses with the TOT method.

To ensure QA/QC and to prove the consistent operation of the instrument, an inner standard, external sucrose aqueous solution and cross method procedure were used. A recovery method was used for the evaluation of the efficiency. Recovery ranged from 96 to 104%, with a standard deviation of < 5%. Recovery was determined by spiking two sets of filters (blank samples and real samples) with a known concentration of carbon. The detection limits were 0.01 µg m⁻³, 0.18 µg m⁻³ and 0.18 µg m⁻³ for EC, OC and TC, respectively (Godec et al., 2016).

PAHs analyses

PAH mass concentrations were determined by extraction with a mixture of cyclohexane and toluene. After centrifugation, solvents were evaporated to dryness in nitrogen. Then, they were redissolved in acetonitrile (Jakovljević et al., 2015, 2016; Pehnc & Jakovljević, 2018; Šišović & Fugaš, 1991). A Varian Pro Star high-performance liquid chromatograph (HPLC) was used for determination of PAHs. Certificate Reference Material (CRM NIST 1649b, Urban dust) was used in order to determine method accuracy and recovery of all PAHs ranging from 90 to 109%. The method detection (DL) and quantification limits (QL) ranged from 0.007 ng m⁻³ for BaA to 0.18 ng m⁻³ for



Fig. 1 Locations of sampling sites in Zagreb

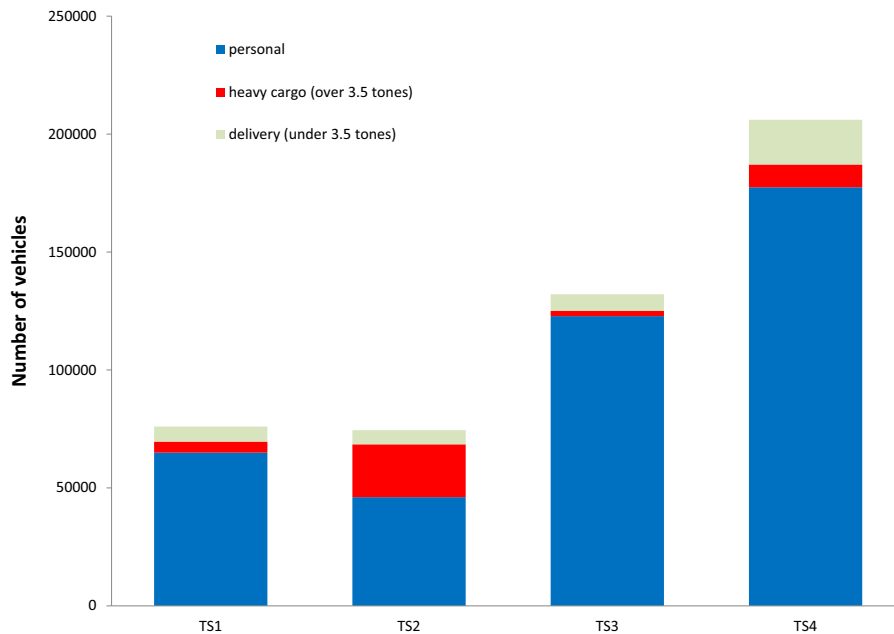


Fig. 2 Numbers of vehicles for all measuring stations

fluoranthene, while the QL for BaP was 0.04 ng m^{-3} (Jakovljević et al., 2015, 2016; Pehnc & Jakovljević, 2018). Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), chrysene (Chry), benzo(a)anthracene (BaA), benzo(e)pyrene

(BeP), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BghiP), dibenzo(a,h)anthracene (DahA) and indeno(1,2,3-c,d)pyrene (IP).

Gas pollutants

Gas pollutants (sulphur dioxide, nitrogen monoxide and dioxide and carbon monoxide—SO₂, NO, NO₂ and CO) were collected with automatic analysers Horiba series 370 for each pollutant separately. Gases were collected according to European standards: EN 14,212:2012 and EN 14,212:2012/AC:2014 for SO₂, EN 14,211:2012 for NO and NO₂ and EN 14,626:2012 for CO. APSA-370 is an ambient sulphur dioxide (SO₂) monitor that uses the ultraviolet fluorescent (UVF) method. APNA-370 is an ambient nitrogen oxide monitor that uses the chemiluminescence (CLD) method. Carbon monoxide (CO) monitor APMA-370 used the non-dispersive infrared analysis method. All automatic analysers allowed continuous measurements of the concentrations of SO₂, NO, NO₂ and CO. The output of the analysers was determined as an hourly value calculated by dividing the measured values acquired every 1 s by 3600 and summing these data for a period of one hour.

Statistical analysis

Statistical analysis was performed using the STATISTICA 13.2 (Tibco Software Inc.) program. For testing the normality of variables, the Shapiro–Wilk test was used. Spatial differences between sites and differences between sampling periods for each measured pollutant were tested by Kruskal–Wallis ANOVA test and *post-hoc* multiple comparison of mean ranks for all groups according to Siegel and Castell. Statistical differences between weekend and working days were tested by Mann–Whitney U test. Statistical significance was set at 5% ($P < 0.05$).

Results and discussion

The measurements were carried out at the following locations: west (TS1), east (TS2), centre (TS3) and south (TS4). These locations were selected in terms of density and volume of traffic, positions in town (west, east, south and centre). Samples were analysed for the following particulate pollutants: PM₁₀, carbon species (OC, EC, TC) and polycyclic aromatic hydrocarbons (PAHs: BaP, Flu, Pir, BaA, Kri, BeP, BbF, BkF, DahA, BghiP, IP) in PM₁₀ and gas pollutants (SO₂, NO₂, CO) in the air related to traffic pollution.

EC/OC and PM₁₀ mass concentrations

Mass concentrations of PM₁₀ particle fraction, elemental carbon, organic carbon, total carbon and the content of organic carbon are shown separately for the weekend (WE-Saturday, Sunday) and working days (WOR). Results are presented in three different times of the day (6 am to 2 pm, 2 pm to 10 pm and 10 pm to 6 am) in Table 1.

At site TS1, the measured PM₁₀ particle concentrations were lower than the limit value, and the weekend values were lower compared to working days. The high mass fraction/content of the total carbon in the PM₁₀ (more than 60% and 40% on weekends and working days) at low values of the OC/EC ratio indicated traffic as the main source of pollution of airborne particles. From Fig. 2, it is evident that personal vehicles mostly predominated at site TS1 (more than 80%). Concentrations of OC during working days were similar during the three measuring periods regardless of a changing number of cars during the days. Concentrations of EC decreased as the numbers of personal cars reduced. The highest values of concentrations of PM₁₀ particles were measured in the morning (6am–2 pm), while the numbers of cars also were the highest. During the day from 2 to 10 pm, PM₁₀ concentrations were the lowest (20.6 µg m⁻³) and then a rise was recorded again during 10 pm and 6am, when the number of cars decreased. The relatively constant concentration of OC and increasing PM₁₀ concentrations during the night (10 pm–6am), when the numbers of cars were lower, indicated that at this measuring site the dominant pollution source during the day was traffic but during the night residential heating. Differences in pollutant concentrations depending on traffic volumes are shown in Fig. S1 of the Supplementary data section. At site TS2, the measured particle concentrations were lower on weekends while working days exceeded the prescribed limit value. The high mass fraction/content of the total carbon in the PM₁₀ (more than 40%) and higher values of the concentration of EC indicates traffic as the one of the dominant sources of pollution by airborne particles, but a high-value OC/EC ratio indicated that an additional portion of organic carbon was derived from other sources of pollution. At site TS2, heavy cargo vehicles exhibited a larger contribution than at TS1 (about 30%). Concentrations of PM₁₀ particles decreased with the

Table 1 Average concentrations of PM₁₀, OC, EC and TC in $\mu\text{g m}^{-3}$ and OC/EC ratio, content of TC in% at all traffic sites

Sampling site	Period of sampling	PM ₁₀	OC	EC	OC/EC	TC	Content TC
TS1	WE 6 _{am} -2 _{pm}	26.1	16.9	0.6	30.7	17.5	67
	WE 2 _{pm} -10 _{pm}	16.2	8.5	2.2	3.8	10.69	66
	WE 10 _{pm} -6 _{am}	18.7	9.9	2.4	4.2	12.3	66
	WOR 6 _{am} -2 _{pm}	31.3	7.4	3.0	2.4	10.4	33
	WOR 2 _{pm} -10 _{pm}	20.6	7.6	2.6	2.9	10.2	50
	WOR 10 _{pm} -6 _{am}	24.4	8.8	1.7	5.2	10.5	43
TS2	WE 6 _{am} -2 _{pm}	23.9	9.6	0.9	9.7	10.6	44
	WE 2 _{pm} -10 _{pm}	33.4	13.7	1.7	8.0	15.4	46
	WE 10 _{pm} -6 _{am}	46.1	19.4	1.4	14.1	20.8	45
	WOR 6 _{am} -2 _{pm}	75.3	24.2	3.2	7.6	24.2	36
	WOR 2 _{pm} -10 _{pm}	54.3	19.4	3.0	6.4	19.4	41
	WOR 10 _{pm} -6 _{am}	44.6	17.9	2.1	8.4	17.9	45
TS3	WE 6 _{am} -2 _{pm}	29.1	10.4	1.2	9.0	11.6	40
	WE 2 _{pm} -10 _{pm}	24.8	9.1	1.3	7.2	10.4	42
	WE 10 _{pm} -6 _{am}	24.8	8.7	1.1	8.0	9.8	40
	WOR 6 _{am} -2 _{pm}	11.8	4.9	1.6	3.1	6.6	56
	WOR 2 _{pm} -10 _{pm}	42.9	12.1	1.7	7.4	13.8	32
	WOR 10 _{pm} -6 _{am}	14.1	4.9	0.9	5.2	5.9	41
TS4	WE 6 _{am} -2 _{pm}	36.2	18.3	3.3	5.5	21.6	60
	WE 2 _{pm} -10 _{pm}	54.3	23.8	7.0	3.4	30.8	57
	WE 10 _{pm} -6 _{am}	58.0	33.4	7.1	4.7	40.5	70
	WOR 6 _{am} -2 _{pm}	63.9	26.4	5.4	4.9	31.8	50
	WOR 2 _{pm} -10 _{pm}	72.5	27.5	6.5	4.3	33.9	47
	WOR 10 _{pm} -6 _{am}	103.8	45.5	6.02	7.6	51.5	50

WE weekend (Saturday, Sunday), WOR working days (Monday-Friday)

number of cars. Differences in pollutant concentrations in correlation with traffic volumes are given in Fig. S2 of the Supplementary data section. At site TS3, the measured particle concentrations were lower than the limit value, and the weekend values were somewhat higher compared to working days. Values of OC/EC ratio indicated that the traffic affected the air more on working days than weekends. At this site, more than 90% was contributed by personal vehicles. The highest value of OC concentrations was recorded during 2 pm and 10 pm, while concentrations of EC were similar during the day but lower during the night. PM₁₀ concentrations were also highest between 2 and 10 pm on working days which indicated that, in addition to traffic, residential heating played an important role in air pollution. Fig. S3 of Supplementary Material shows differences in concentrations of pollutants under varying traffic volumes. At site TS4, the measured concentrations of particles during the weekend were near the limit value, while on working

days they were significantly higher than the prescribed limit value. At this measuring site, the numbers of vehicles were higher than at all other sites and more than 85% accounted for personal automobiles. The content of organic carbon was higher during weekends than working days, while the concentrations of elemental carbon were high and uniform. Values of OC/EC ratio pointed toward traffic as a significant source of pollution by atmospheric particles. The highest value of OC concentrations during working days were recorded at night ($45.5 \mu\text{g m}^{-3}$), while concentrations of EC were similar throughout the measuring period. Concentrations of PM₁₀ particles increased during the day and the highest value were recorded at night from 10 pm to 6am (Fig. S4). At this measuring site, the dominant sources of pollution were traffic in the morning but residential heating had an important role during the rest of the day. At each site, the measured concentrations of PM₁₀ differed during the working days and weekends, only on site TS3 were

the mass concentrations of PM₁₀ lower during working days compared to weekends. The highest concentrations of PM₁₀ were recorded during working days in the south (TS4) and west (TS2) of the city, but at different periods of the day.

Statistical differences were tested between sampling sites, and differences were found for concentrations of PM₁₀ and OC between TS1 and TS4 ($P < 0.05$) and for concentrations of EC ($P < 0.001$), OC and PM₁₀ ($P < 0.05$) between TS3 and TS4. For concentrations of EC, OC and PM₁₀ no statistical differences were found between sampling periods during one day, but between the weekend and working day, a marginal statistical significance was concentrations of EC at site TS2 and for PM₁₀ at site TS4.

The concentration of OC in this study was higher than in Manoli et al., (2016) for urban traffic and in Keuken et al. (2013) for a street location, but the EC concentration was lower. Hak et al. (2010) measured the PM₁₀ particle fraction at a traffic and background site. At both locations, the concentration was lower than in our study. Chow et al. (2002) measured OC, EC and TC in Mexico City and found lower concentrations than in this study except at site TS3 where the concentrations were lower than those measured in Mexico City. Compared to a previous study conducted at a canyon traffic site in Zagreb (Šimić et al., 2020), values of EC were similar to those measured at TS1, TS2 and TS3, but much lower than those measured at TS4. OC values at sites TS1 and TS3 were similar, but much higher at TS2 and TS4.

PAH mass concentrations

Mass concentrations of PAHs are shown in Table 2 where the results are presented separately for the weekend (WE-Saturday, Sunday) and the working days (WOR) at three different times of the day (6 am to 2 pm, 2 pm to 10 pm and 10 pm to 6 am). The highest concentrations of all PAHs were measured at site TS4, and the lowest at site TS1.

At site TS1 and TS2, the concentrations of all measured PAHs decreased during the day and the highest values were mostly recorded during the morning at a time when the numbers of delivery and heavy cargo vehicles were the highest.

At TS3, the highest value of PAH concentrations was measured during 2 pm and 10 pm on working

days, probably because this site was near a bus stations and the number of arrivals and departures of bus was increased. At site TS4, the highest values during work days were recorded at night (10 pm-6am), as this site is a large residential area and PAH concentrations can also come from residential heating. Differences between pollutant concentrations under traffic volumes for all measuring sites are shown in Fig. S1-S4 of the Supplementary data section.

The highest concentrations of all of the measured PAHs were recorded on working days in the south of Zagreb (TS4) over the period from 10 pm to 6 am. The mass concentrations of all of the measured PAHs except for Flu were higher during working days than on weekends in the east (TS2) and south (TS4) of the city.

For concentrations of Flu and Pyr, a statistically significant difference was not found between the sampling sites, while for the rest of PAH concentrations statistically significant differences were found. Differences for each PAH were found between TS1 and TS4 ($P < 0.05$) except for DahA where a difference was found between TS1 and TS2 ($P < 0.05$). For BeP and BghiP concentrations, differences were also found between TS2 and TS4 ($P < 0.05$), but for IP the differences were statistically also significant between TS3 and TS4 ($P < 0.05$). Concentrations of PAHs in different sampling periods were not statistically significant, but between weekends and working days the concentrations were only marginally statistically significant (for Flu, BaA and IP at site TS1, BaA, Chry, BaP and BghiP at site TS2, and for DahA and IP at site TS4).

PAH concentrations related to traffic (BghiP, IP and DahA) at site TS1 and TS3 were similar to previous studies at Zagreb, but concentrations of PAHs (BghiP, IP) showed increased values at site TS4 and slightly higher values of BghiP on site TS2 (Jakovljević et al., 2015; Šišović et al., 2012). Concentrations of PAHs with four aromatic rings were lower than PAHs with five or more aromatic rings at all locations. Flu and Pyr (lighter PAHs with lower molecular mass, four aromatic rings) mostly originated from domestic heating or wood combustion (Agudelo-Castañeda et al., 2014; Teixeira et al., 2012; Chang et al., 2006), and they can evaporate easily from particles, which makes them more sensitive to meteorological conditions than other PAHs (Galarneau, 2008). Manoli et al., (2016) investigated concentrations of

Table 2 Average concentrations of polycyclic aromatic hydrocarbons in ng m⁻³ at all of the traffic sites

Sampling site	Period of sampling	Flu	Pyr	BaA	Chry	BeP	BbF	BkF	BaP	DahA	BghiP	IP
TS1	WE 6 _{am} -2 _{pm}	0.61	0.72	0.35	0.58	0.56	0.85	0.32	0.54	0.00	2.17	0.84
	WE 2 _{pm} -10 _{pm}	0.48	0.35	0.16	0.24	0.27	0.45	0.20	0.35	0.00	1.21	0.55
	WE 10 _{pm} -6 _{am}	0.51	0.52	0.21	0.31	0.33	0.77	0.33	0.60	0.17	2.14	0.68
	WOR 6 _{am} -2 _{pm}	1.16	1.32	0.58	0.53	0.00	0.91	0.36	0.56	0.00	2.44	1.65
	WOR 2 _{pm} -10 _{pm}	1.09	0.63	0.61	0.51	0.00	1.02	0.45	0.61	0.00	1.88	1.75
	WOR 10 _{pm} -6 _{am}	0.74	0.50	0.40	0.31	0.54	0.79	0.33	0.40	0.00	2.46	0.94
TS2	WE 6 _{am} -2 _{pm}	0.45	0.31	0.18	0.30	0.26	0.70	0.26	0.44	0.12	2.28	0.64
	WE 2 _{pm} -10 _{pm}	2.86	2.01	1.50	1.78	1.59	4.05	1.27	2.68	0.91	10.46	2.86
	WE 10 _{pm} -6 _{am}	2.03	2.27	1.49	1.73	1.67	4.67	1.50	2.71	1.02	11.35	3.37
	WOR 6 _{am} -2 _{pm}	2.55	2.98	1.70	2.14	1.77	5.64	1.84	3.84	0.80	14.43	3.54
	WOR 2 _{pm} -10 _{pm}	1.05	1.87	1.81	2.18	1.84	4.99	1.78	3.58	0.90	14.61	3.38
	WOR 10 _{pm} -6 _{am}	1.65	1.51	1.70	1.91	1.58	4.62	1.49	3.42	0.98	13.10	3.14
TS3	WE 6 _{am} -2 _{pm}	0.86	1.50	0.83	1.75	0.74	2.40	1.09	1.92	0.93	6.80	1.46
	WE 2 _{pm} -10 _{pm}	1.08	1.03	0.63	1.45	0.65	2.00	1.07	1.61	0.33	5.34	1.26
	WE 10 _{pm} -6 _{am}	0.83	0.84	0.52	1.18	0.67	1.83	0.76	1.15	0.27	4.30	1.05
	WOR 6 _{am} -2 _{pm}	0.72	0.41	0.29	0.64	0.32	0.88	0.41	0.65	0.13	2.44	0.56
	WOR 2 _{pm} -10 _{pm}	1.86	1.91	1.22	2.38	1.49	3.20	1.17	2.03	0.81	7.99	1.86
	WOR 10 _{pm} -6 _{am}	0.47	0.49	0.22	0.40	0.00	0.60	0.25	0.23	0.00	1.36	0.64
TS4	WE 6 _{am} -2 _{pm}	0.38	0.14	0.58	1.94	0.68	2.69	1.06	1.53	0.31	5.60	1.26
	WE 2 _{pm} -10 _{pm}	2.54	1.49	2.54	4.15	1.49	4.98	2.20	4.05	0.00	11.69	4.02
	WE 10 _{pm} -6 _{am}	2.63	2.20	4.18	6.22	1.86	5.69	2.94	6.31	0.00	18.66	4.42
	WOR 6 _{am} -2 _{pm}	1.57	1.94	3.11	5.06	1.36	5.20	2.25	3.56	0.68	12.59	5.50
	WOR 2 _{pm} -10 _{pm}	1.78	1.55	4.43	6.19	1.98	7.13	3.11	5.76	2.75	16.36	5.60
	WOR 10 _{pm} -6 _{am}	4.88	4.33	7.26	10.78	3.61	15.05	5.08	14.62	0.94	30.81	10.42

WE weekend (Saturday, Sunday), WOR working days (Monday-Friday)

PAHs at urban traffic (UT) and urban background (UB) sites. They found that at the urban traffic sites the concentration of BaP was higher during the warm and cold period than at the urban background (warm UB 0.002 ng m⁻³, warm UT 0.12 ng m⁻³, coldUB 0.7 ng m⁻³, coldUT 0.86 ng m⁻³). Concentrations in our study were higher at all sites except at site TS1 where concentrations were lower than in Manoli et al. (2016). Hak et al. (2010) reported the concentration values as minimum and maximum at traffic and urban background sites. The concentration of BaP was 0.1 ng m⁻³ which was much lower than the concentrations measured in our study. Compared to Sarajevo (Pehnc et al., 2020), the values in our study on all TS were lower.

The diagnostic ratios of PAHs can be used to identify possible pollution sources (Cazier et al., 2016;

Hanedar et al., 2014; Jakovljević et al., 2015, 2016; Kuo, Chen, et al., 2012; Pehnc & Jakovljević, 2018; Šišović et al., 2012; Teixeira et al., 2012; Yunker et al., 2002; Zhang et al., 2004). Figure 3 shows the diagnostic PAHs ratios (Flu/(Flu + Pyr), IP/(IP + BghiP), BaP/BghiP and BaP/(BaP + Chry)) at all of the sites. A Flu/(Flu + Pyr) ratio lower than 0.5 is characteristic for gasoline combustion (Cazier et al., 2016; Hanedar et al., 2014; Jakovljević et al., 2015, 2016; Pehnc & Jakovljević, 2018; Šišović et al., 2012; Yunker et al., 2002). BaP/BghiP ratio values between 0.3 and 0.78 are typical for cars (Hanedar et al., 2014; Teixeira et al., 2012). Values of 0.33 for the BaP/(BaP + Chry) ratio indicated vehicles with a catalyst, 0.5 diesel, and 0.73 gasoline (Cazier et al., 2016; Hanedar et al., 2014; Jakovljević et al., 2015, 2016; Pehnc & Jakovljević, 2018;

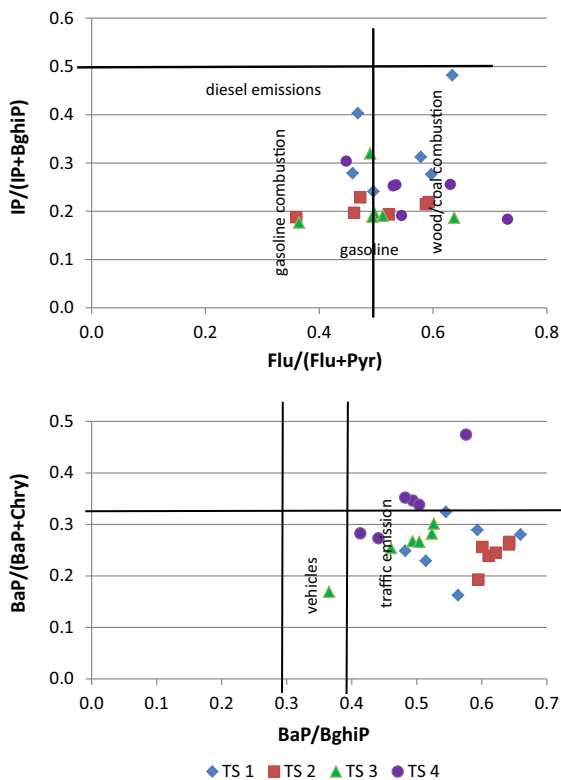


Fig. 3 The diagnostic ratio of the PAHs at all traffic sites

Šišović et al., 2012; Teixeira et al., 2012; Yunker et al., 2002; Zhang et al., 2004). At all of the sites, the Flu/(Flu + Pyr) ratios ranged from 0.4 to 0.7 which pointed to wood burning as the possible source (Fig. 3), but the IP/(IP + BghiP) ratio was between 0.2 and 0.5 at TS1, 0.2 at TS2, 0.2 and 0.3 at TS3 and TS4, respectively. This value indicated vehicle emission (diesel) as a major source at all of the sites. At all of the measuring sites, personal automobiles were the predominant type of cars, but at TS2 30% were heavy cargo vehicles, and at site TS4 delivery vehicles (about 10%) were more frequent than heavy cargo cars (less than 5%) (Fig. 2). At all measuring sites, the BaP/BghiP ratio ranged from 0.2 to 0.5, a value characteristic for cars emission. The general conclusion is that traffic was a significant source of PAH pollution in the nearby area.

Gaseous pollutants

Anthropogenic activity is considered to be accountable for the main sources of gaseous pollutants in the

air (Kampa & Castanas, 2008). We investigated the concentrations of gaseous pollutants (CO, NO₂, SO₂) to characterize urban traffic air pollution in Zagreb. Average hourly values of concentrations of gases pollutants are shown in Fig. 4.

Concentrations of pollutants related to traffic (CO and NO₂) showed high value concentrations in the morning between 8 and 9 am and in the afternoon they increased after 4 pm with maximal values during 8–10 pm at sampling site TS1 (Fig. 4). Concentrations of CO and NO₂ showed high values between 10 and 12 am and maximal values between 9 pm and 2 am at sampling site TS2 (Fig. 4). SO₂ concentration showed much lower maximums for 8–9 am and 3–6 pm at both sites, at this measuring period the number of cars were the highest, and it is evident that concentrations of NO₂ and SO₂ were in relation with the number of cars (Fig. S1 and S2). Overall, SO₂ levels were low. At sampling site TS3, CO concentrations were similar throughout the day, while NO₂ concentrations showed a high value in the morning period between 10 and 12 am, and in the evening between 6 and 11 pm. SO₂ concentrations showed an increasing concentration in the afternoon and evening, with a large waste of results (Fig. 4). At sampling site TS4, concentrations of CO and SO₂ were similar throughout the day, while NO₂ concentrations showed a high value at morning between 11 am and 12 pm, and in the afternoon they increased after 4 pm with maximal values during 9–10 pm (Fig. 4). The differences of gaseous pollutants concentrations under the traffic volume were similar at all measuring area and are shown in Fig. S1–S4 of the Supplementary data section.

Statistical differences were not found for NO₂ concentrations between sampling sites, but for CO concentrations ($P < 0.05$) and SO₂ ($P < 0.001$) statistical differences were found between TS1 and TS3 and for concentrations of CO also between TS3 and TS4 ($P < 0.05$). Statistical differences between different sampling periods were not found for any gas pollutants, and differences between weekends and working days were marginally statistically significant for concentrations of NO₂ and SO₂ at site TS2.

Dependences of gaseous pollutants on wind direction are shown in Fig. 5 for all sampling sites. At sampling site TS1, high concentrations of CO and NO₂ were recorded during the north wind, while the SO₂ concentrations were independent of wind direction. At sampling site TS2, wind roses showed a high

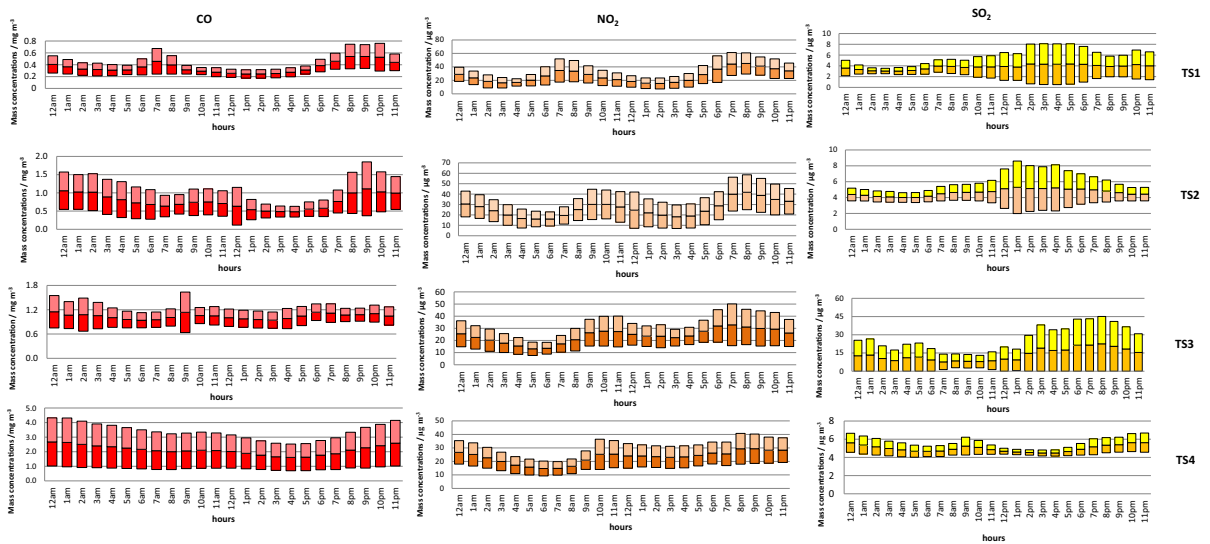


Fig. 4 Average hourly values of mass concentrations (mean ± standard deviation) of CO, NO₂ and SO₂ at TS1-TS4

concentration of CO which was recorded during the southeast wind, while the SO₂ and NO₂ concentrations were independent of the wind direction with a slight increase following wind from the north-northwest direction. At sampling site TS3, a high concentration of NO₂ was recorded during the west wind, and concentrations of SO₂ were recorded during the northeast wind, while the CO concentrations were independent of the wind direction. At sampling site TS4, concentrations of CO, and NO₂ were independent of the wind direction, while a higher SO₂ concentration was recorded during the southwest wind.

Human exposure

The toxicity of most carcinogenic PAH is associated with the particle phase rather than the gas phase (Lyll et al., 1988). Human exposure to PAHs is complex for several reasons. Only a few papers have involved human epidemiological studies on individual PAHs, and a mixture of PAHs may be even more carcinogenic to humans than individual PAHs (Van Houdt et al., 1987). The most studied PAH is benzo(a)pyrene, while other PAHs have mostly been characterised with regard to their cancer potency by the toxic equivalence factor (TEF). Combinations of TEFs and WHO quantitative risk assessment methodology can be used for estimation of lung cancer due to PAH exposure. However, the use of these factors does not take into

account differences mainly due to age. Potential human carcinogenic risk related with chemical exposure is given to increased possibility of developing cancer through a person’s lifetime. Human health risks depend on the inhaled amount of contaminant, the extent of exposure and the toxic effects of the contaminant. In this study, risk assessments were calculated for people who lived near these locations and spent their free time outdoors. Risk was calculated according to EPA (2011) methodology and Amarillo et al., (2014) using linear Eq. (1). LADD is the long-lasting daily intake of carcinogen complex and can be calculated from the concentration of compound (CA) and intake factor (IF), Eq. (2).

$$\text{Risk} = \text{LADD} \times \text{SF} \tag{1}$$

LADD—Life Averaged Daily Dose/mg kg⁻¹ day⁻¹, SF—slope factor/kg day⁻¹ mg⁻¹

$$\text{Risk} = \text{CA} \times \text{IF} \times \text{SF} \tag{2}$$

CA—concentration of compound/mg m⁻³, IF—intake factor/m⁻³ kg⁻¹ day⁻¹.

The intake factor was calculated from age-specific physiological and exposure parameters, Eq. 3.

$$\text{IF} = \frac{IR_a \times ED \times EF \times ET}{BW \times AT} \tag{3}$$

BW—body weight/kg, IR_a—breathing rate/ m³ h⁻¹, EF—exposure frequency, number of exposure per year, ED—duration of exposure in years, ET—

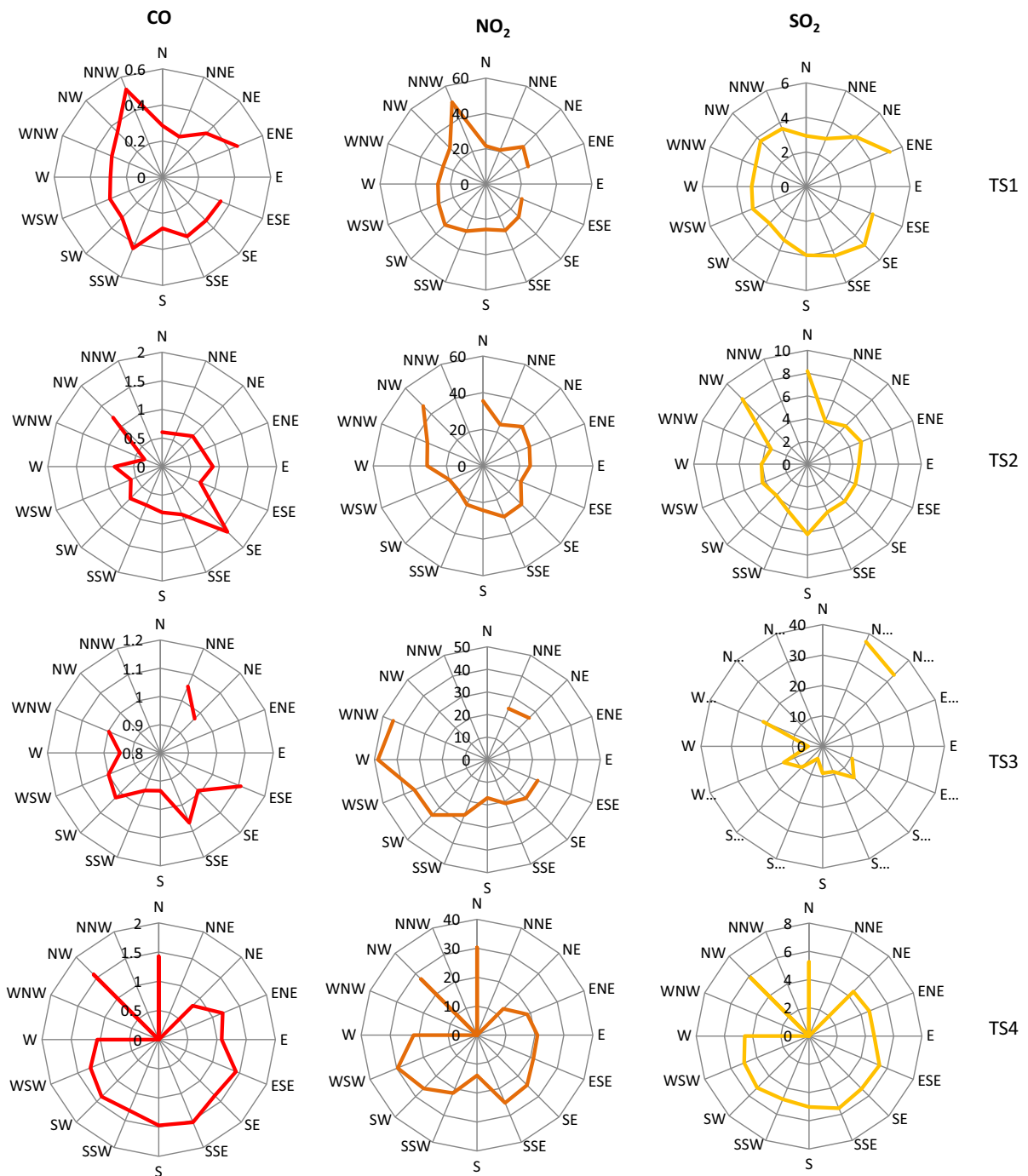


Fig. 5 Wind roses for CO (mg m^{-3}), NO₂ ($\mu\text{g m}^{-3}$) and SO₂ ($\mu\text{g m}^{-3}$) of TS1, TS2, TS3 and TS4

exposure time, number of hours per exposure, AT—averaging time, average exposure extent over a lifetime.

SF is an estimation of the probability of the response per unit chemical intake over a person's lifetime. The SF is a result of inhalation unit risk (IUR), body weight (BW) and breathing rate

expressed as $m^3 \text{ day}^{-1}$ (IR_b). The IUR values used in this study for risk assessment are reported in Table S1 of the Supplementary data section.

$$\text{Risk} = CA \times \left(\frac{IR_a \times EF \times ED \times ET}{BW \times AT} \right) \times \left(\frac{IUR \times BW \times 1000}{IR_b} \right) \quad (4)$$

IR_b —breathing rate/ $m^3 \text{ day}^{-1}$.

To calculate health risk, we used parameters from the EPA (2011) and Amarillo et al. (2014). The risk level of the possibility of developing cancer was determined for peoples who spent 5 h per day outdoors, over a lifetime of 76 years and body weight 80 kg. Exposure frequency was taken during 350 days per year. Results of estimated health risks are shown in Fig. 6. Values of the parameter used in calculating risk are shown in Table S2 of the Supplementary data section. To estimate health risks for populations who lived in the study area, the main limitation was that a single city is insufficient and the internal exposure dose cannot be measured because the IF was taken from Amarillo et al., (2014).

The highest risk was observed at TS4, with highest values during working days. At TS3, the measured site health risk values were higher on working days between 2 and 10 pm, but high values were also found on the weekend, this value was higher than on working days after 10 pm. Statistically significant differences were not found between sampling sites for health risk based on Flu and Pyr concentrations but were for the remaining PAHs. Differences for each PAH health risk were found between TS1 and TS4 ($P < 0.01$) except for DahA where a difference was found between TS1 and TS2 ($P < 0.01$). For BghiP, differences were also found between TS2 and TS4 ($P < 0.01$), but for IP the differences were statistically significant also between TS3 and TS4 ($P < 0.05$). The health risk from PAHs in different sampling period was not statistical significant, but between weekends and working day marginal statistical significance was found for Flu, BaA and IP at site TS1, BaA, Chry, BaP and BghiP at site TS2, and for DahA and IP at site TS4. At measuring sites TS1 and TS2, no significant differences between weekend and working days were found. As for the individual toxicity of the PAH, the highest contributor to the total estimated risk was BaP.

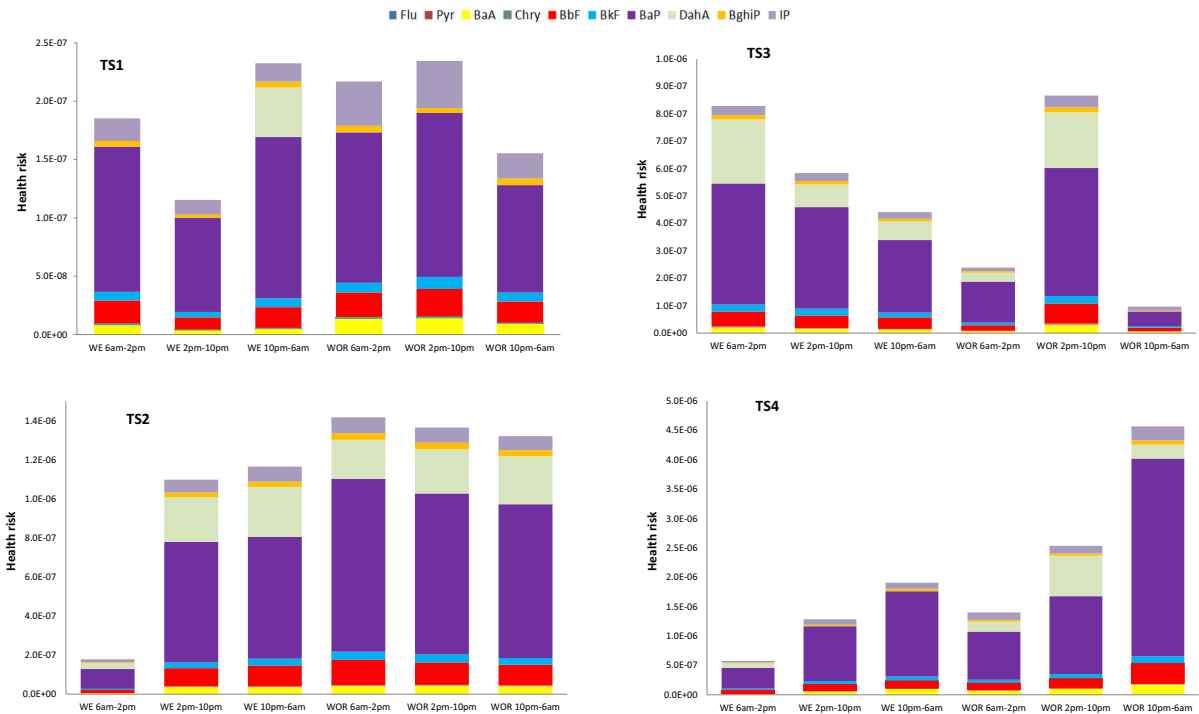


Fig. 6 Average estimated lifetime lung cancer risk per person exposed, by PAH and period of day

A study conducted in Argentina reported human health risks based on seasons, and these values were several orders of magnitude higher than those in the present study (Amarillo et al., 2014), but the values reported for a Western Balkans site were similar to those presented here (Bartoš et al., 2009). The results calculated in this study were slightly lower than at an urban site in Teheran situated near traffic (Jaafari et al., 2019). These authors measured PAHs in PM₁₀ particles and calculated carcinogenic risk via inhalation. They found no differences for cancer risk between the urban and rural site. Results shown by Baek et al. (2020) for a residential site (Pohang city, South Korea) were also higher than results for cancer risk in this study. They found that PAH groups contribute 42.1% to the cumulative cancer risk at the residential site. Sari et al. (2020) calculated a health risk assessment for two groups: children and adults. Their results were higher than the results calculated in this study. Carcinogenic risk was also calculated in Shen et al., (2020) for two groups (adult and children) via inhalation, ingestion and dermal exposure. Results of the risk via inhalation are comparable with the results obtained in the present study. Shen et al., (2020) explained that human exposure via dermal and ingestion had an important role in their risk assessment, but we gave focus to only exposure via inhalation because this is the main pathway of airborne toxic compounds to the human body. Another limitation was the fact that in this study only PM particles were sampled and gaseous PAHs were not included. For a better risk assessment, the concentration of gaseous PAHs may be taken into calculation. Risk assessments via inhaling on PAHs bounded to PM particles can be useful for better quantifying the cancer risk connected with air pollution.

Previous research described that, however, the concentrations of 3- and 4-ring PAHs high, health risks were mostly related with particulate phase 5- and 6-ring PAHs. According to the EPA (2003) and Chen and Liao (2006), exposures for which the risk factor exceeds 1×10^{-6} are scored as significant (e.g. one occurrence in 1 million people). Risk values from 1×10^{-6} to 1×10^{-4} point to a probable human carcinogenic risk, and values above than 1×10^{-4} point to serious carcinogenic risk. The results of this study have shown that human health risk was several magnitudes lower than 1×10^{-6} in the west and in the centre of Zagreb. In the eastern part of town, human

health risk was very close to 1×10^{-6} , but in the south of Zagreb, health risk sometime exceeded the value established by the EPA (2003). This implies that there is a risk that one person per million could fall ill with cancer due to exposure to PAHs.

Conclusion

Measurements of air pollutants (CO, SO₂, NO₂, PM₁₀, OC, EC and PAHs bound to PM₁₀) carried out at four crossroads in Zagreb, Croatia, showed statistically significant differences between sampling sites for all pollutant concentrations, except for NO₂. The highest mass concentrations of PM₁₀, elemental and organic carbon and PAHs were found in the south of the city, characterized with the largest crossroads and the highest traffic density, while the lowest concentrations of PM₁₀ were recorded in the east and centre of town. PM₁₀ samples were collected over three periods (6 am to 2 pm, 2 pm to 10 pm and 10 pm to 6 am) on working days and weekends in order to determine diurnal and weekly variations. Concentrations of gasses related to traffic (CO and NO₂) showed high values in the morning and afternoon when they increased after 4 pm with maximal values during evening in the west and east of town. PM₁₀ and PM₁₀ bounded organic compounds at all of the measuring sites also had the highest concentrations during morning and afternoon period; however, at measuring site in the south high PAH concentrations were recorded during night which indicated that residential heating had a role as a pollution source. The highest concentrations of PM₁₀ were recorded during working days in the west and south part of town, but at different periods of the day. In the centre of Zagreb, mass concentrations of OC were higher on weekends compared to working days. At the west and south part of town, concentrations of OC and EC were higher on working days than on weekends. However, for all measured pollutant concentrations differences between parts of the days were not found statistically significant, but between working days and weekends were marginally statistically significant for some pollutants.

In general, traffic was found to be an important source of air pollution in the investigating areas, although the influence of other sources such as residential heating was also noticed at some locations.

The estimated health risk factor was close to 1×10^{-6} in the east and exceeded that value at the southern part of town, which was scored as significant risk by the EPA (2003). The results regarding human health risk should be taken with caution because only inhalation was taken into consideration, and ingestion exposure via food or water consumption may also be significant.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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