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Levels of PM$_{10}$-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation

Mirjana Perišić[1] · Slavica Rajšić[1] · Andrej Šoštarić[2] · Zoran Mijić[1] · Andreja Stojić[1]

Abstract The aim of this study was to identify levels of population health risk caused by the inhalation of PM$_{10}$-bound species in an urban area. A combination of multiple location measurements, several analytical tools, and cancer and non-cancer health risk assessment was used to evaluate influences of proximate anthropogenic activities and air pollution transport. The concentrations of PM$_{10}$, six trace metals (As, Cd, Cr, Mn, Ni and Pb) and benzo[a]pyrene were measured at 15 air quality monitoring stations during the period 2011–2015 in a wide area of Belgrade (Serbia). Significant population health risk was estimated as a result of exposure to particulate air pollution. The concentrations of PM$_{10}$, As, Ni and benzo[a]pyrene exceeded the EU Directive limit and target values. Of all the analysed species, Cr was the major contributor to carcinogenic health risk. Besides strong local sources related to traffic and industry, the influence of transported pollution is estimated in the range 8.95–36.07 %, with potentially the most important sources being located in East and West Europe.

Keywords Health risk · PM$_{10}$ · Trace metals · Transport

✉ Mirjana Perišić
   mirjana.perisic@ipb.ac.rs

[1] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

[2] Institute of Public Health Belgrade, Bulevar Despota Stefana 54, 11000 Belgrade, Serbia

Introduction

Particulate matter with an aerodynamic diameter of less than 10 μm (PM$_{10}$) has been recognised as a threat to public health on a global scale (WHO 2013; Fuzzi et al. 2015). Epidemiological studies suggest a strong exposure–response correlation between ambient concentrations and short- (hospital admission and premature mortality) and long-term (lung cancer and cardiovascular and immunological diseases) health effects (Valavanidis et al. 2008; Anderson et al. 2012; Stanišić Stojić et al. 2015). Of the entire population, children represent the most sensitive group due to their rapid growth and development of the lungs and immune systems (Mathew et al. 2015; Zhanghua et al. 2015). The composition of PM$_{10}$ varies greatly and depends on many factors, but in urban areas, transition metals, ions (sulphate and nitrate) and organic compounds represent the major components. Numerous studies have indicated that some of the PM-bound species induce very harmful health effects (An et al. 2013; Pandeya et al. 2013; Szabó et al. 2015), noting that the inhalation of chromium-containing aerosols is one of the major concerns (Langard and Costa 2014; Laulicht et al. 2014). This element is emitted to the environment during various natural and anthropogenic activities in mainly two oxidation states: trivalent and hexavalent, where Cr(VI) is considered as more toxic due to its high solubility and mobility. It is a well-reported occupational carcinogen associated with lung, nasal and sinus cancers (Mishra and Bharagava 2016). Likewise, the International Agency for Research on Cancer (IARC 1990) recognised that almost all nickel compounds have been classified as human carcinogens. Based on epidemiological studies, following inhalation exposure, the respiratory system is the primary target of nickel toxicity (Schaumloffel 2012). Several reports from the United States Environmental Protection Agency (USEPA 2011a, 2015) have considered cancer risks caused by the inhalation of nickel compounds emitted by large oil combustion and

petroleum refining sources. Arsenic compounds threaten the gastrointestinal tract, circulatory system, liver, kidney and skin (EA 2008; Pushan et al. 2007), whilst benzo[*a*]pyrene (BaP), a well-known polycyclic aromatic hydrocarbon, may cause respiratory tract irritation, damage of the reproductive system and different types of cancer (Kim 2013). BaP is emitted from the incomplete combustion of various fuels, and according to AQE (2015), the main sources of this compound are domestic heating, coal burning and road traffic. Compounds with cadmium are primarily toxic to the kidneys and also cause bone demineralisation, but in polluted industrial areas, excessive exposure to airborne Cd may impair lung function and increase the risk of lung cancer (Bernard 2008). Cadmium is a component of petrol and diesel fuel, and alloyed with copper, it is used in the production of car radiators and car paints (ANPI 2015). In an urban environment, cadmium-laden ultrafine dust occurs in close proximity to busy roads as a result of vehicles, road surface wear and vehicular fuel emissions (Murphy and Hutchinson 2015). Also, an important source of cadmium compounds are coal combustion processes, whether heating in houses or electricity production in industrial areas (Flagan and Seinfeld 2012). Manganese is released to the environment from anthropogenic (industry, fossil fuel combustion and traffic) and natural emission sources (volcanic eruptions and erosion of manganese-containing soils). Evidence for the neurotoxic effects of environmental manganese on children is increasing and includes associations with cognition, memory, behaviour and motor function (WHO 2004). Some epidemiological studies have also examined manganese–lead interaction in early childhood, a period of potentially heightened susceptibility to neurotoxins (Henn et al. 2012). On the other hand, besides anaemia and reproductive problems, exposure to higher lead concentrations can severely damage the brain and kidneys in adults or children and ultimately cause death. The USEPA (2006) classified lead and inorganic lead compounds as 'probable human carcinogens'.

Like most metropolitan areas, Belgrade (Serbia) has significant air pollution problems, mainly as a result of high population density (the average is 3241 people/km^2: AQP 2015) and the accumulation of major economic activities in the region (Rajšić et al. 2008; Mijić et al. 2012; Stojić et al. 2015a). SE Belgrade, about 30 km from the city centre, is home to several industrial facilities, including the largest thermal power plants, Nikola Tesla A and B, and Kolubara A, and the largest lignite coal basins in Serbia. The production capacity of these plants is greater than 50 % of the electricity used in Serbia and, with the coal basin, represents important sources of air pollution in the Belgrade suburban area. Coal mine and combustion processes are characterised by the emission and resuspension of large amounts of particulate dust, which, in the case of the exploitation of lignite, contain a significant portion of arsenic compounds (Jamshed et al. 2015). In the suburban parts of Belgrade, arsenic and BaP are the products of incomplete combustion of fossil and solid fuels, despite the removal of a large number of individual

heating units and the transition to a distant heating system in recent years (Perišić et al. 2015). In the municipality of Rakovica, 10 km away from the centre, a large foundry for metal casting production is located, representing the main source of air pollution, especially for heavy metals, in this area.

Generally, the use of outdated technologies in all production sectors, rise in the number of vehicles and the transport of pollutants from neighbouring industrial countries have led to a severe degradation of air quality in the last two decades in Belgrade (Stojić et al. 2016). According to the Environmental Quality Report (EQR 2014), for the period 2000–2013, the number of days with the average PM$_{10}$ concentrations higher than the daily limit values of 50 μg m^{-3} proposed by EU Directive 2008/50/EC was in the range of 21–345 (at different locations). Because human health represents the main concern in the regulation of urban air quality, the important question is to what extent people are actually exposed to the observed pollution levels.

This study presents analysis of the 5-year data (2011–2015) of PM$_{10}$ and PM$_{10}$-bound trace metals (As, Cd, Cr, Mn, Ni and Pb) and BaP concentrations in the greater Belgrade area from 15 representative monitoring stations of different types. The measured concentrations and toxicity information were used to characterise the distribution of cumulative cancer and non-cancer health risks, in accordance with the USEPA health risk assessment model (USEPA 2005, 2013) and the California Environmental Protection Agency (CalEPA) Air Toxics Hot Spots Program (CalEPA 2003, 2008). The CalEPA model was used to consider the exposure of the population in different age stages. In recent years, the World Health Organization (WHO) reports have emphasised that transport of particulate matter (PM) contributes significantly to exposure and to health effects (WHO 2006). In order to identify the impact of potential remote emission sources to air pollution in the Belgrade area, advanced trajectory ensemble models (TEMs) were applied based on PM$_{10}$ and trace metal data.

Materials and methods

Sampling sites

With 22.5 % of the country's population, Belgrade represents the largest urban area in the Republic of Serbia and, with 1.6 million citizens, the second largest urban centre in the Balkans. It is located at the confluence of two international waterways and represents an important regional traffic core of connections between Eastern and Western Europe. In this study, data of ambient daily PM$_{10}$ concentrations and corresponding species were obtained from 15 monitoring stations of the Air Pollution Monitoring Network supervised by the Institute of Public Health of Belgrade (IPHB). The measurements were conducted at 11 urban, 2 suburban industrial and 2 rural industrial stations (Fig. 1 and Electronic supplementary

material (ESM) Table S-1). Urban stations are mainly located in the city centre, in densely populated zones with heavy and slow traffic. All common forms of public transportation—buses, trolleybuses and trams—are in use, and the route of the international highway E75 passes through the city. The total number of vehicles in the city consists of approximately 40,000 passenger vehicles, 1000 diesel-fuelled city buses, 400 heavy-duty trucks, 108 trams and 76 trolleys per day (Vuković et al. 2015). ESM Fig. S-1 represents the traffic scenario in Belgrade with the main routes and traffic areas. The suburban industrial area is under the influence of intensive industrial activities—the largest coal basin in Serbia, Kolubara, and three large thermal power plants (Nikola

Tesla A, TENT A; Nikola Tesla B, TENT B; and Kolubara A)—located about 30 km S–SW from the city centre (ESM Fig. S-2). Rural industrial sites, VC and GR, are located near the coal basin, as well as ash disposal in the electricity production area (Fig. 1). In order to illustrate the primary land use in Belgrade, in ESM Fig. S3, the main industrial areas, agricultural lands, residential areas and urban cores are presented.

Sampling and analysis

The analysed dataset includes PM_{10} mass concentrations, obtained by means of reference Sven Leckel samplers, and daily concentrations of trace metals (As, Cd, Cr, Mn, Ni and Pb) and BaP determined by the use of reference methods: gas chromatography mass spectrometry (Agilent GC 6890 MSD 5975) and inductively coupled plasma mass spectrometry (Agilent 7500) according to standards EN 12341[1] and EN 14902[2], respectively. Values below the method detection limits were replaced by 1/2DL. Details of the measurement methodology, as well as the accuracy and precision of the detection methods, are presented in ESM Table S-1.

Statistical analysis

Basic statistical and trend analyses of measured species were performed by the use of the 'openair' package (Carslaw and Ropkins 2012). The Theil–Sen method within the package Median Based Linear Models ('mblm') was used for trend analysis of the measured concentrations. Deseasonalised time series were obtained using the function SmoothTrend implemented in the 'openair' package. The relative importance of each measured variable to the prediction of PM_{10} mass concentrations, which enabled a better insight into PM_{10} sources, was determined by the use of the 'randomForest' package (Liaw and Wiener 2002). An appropriate number of trees was determined to assure out-of-bag error convergence (i.e. an unbiased internal error estimate of the prediction error) in order to stabilise the error and avoid overfitting. In order to evaluate the temporal distribution and seasonal pattern of the measured variables, the non-parametric probability density function (PDF) was performed with the 'ggplot2' package (Wickham and Chang 2015). The procedure assumes dispersion of the mass of the empirical distribution function over a regular grid and then uses the fast Fourier transform to convolve this approximation with a discretised version of the kernel. Subsequently, a linear approximation is applied to evaluate the density at the specified points. All of the aforementioned packages were implemented in the statistical software environment R (Team RC 2012).
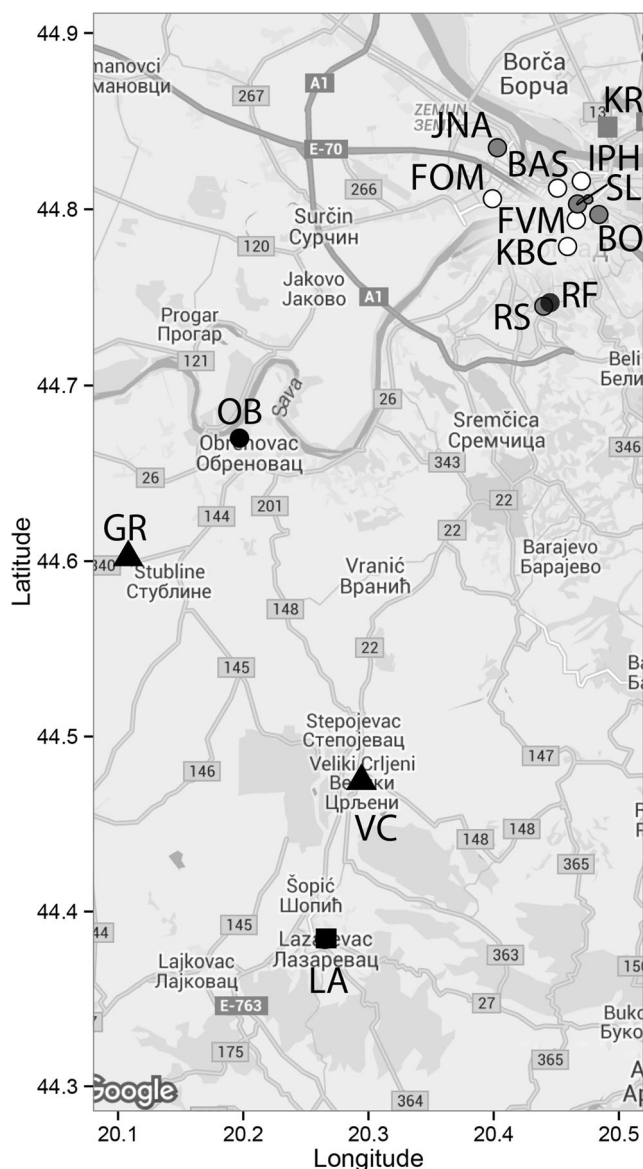

Fig. 1 Sampling site locations in the Belgrade city metropolitan area: urban (*circles*); suburban industrial (*squares*); rural industrial locations (*triangles*); locations exposed to traffic (*white*); traffic and heating (*grey*); and locations near industrial sources (*black*)

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[1] Determination of the PM_{10} fraction of suspended particulate matter—reference method and field test procedure to demonstrate reference equivalence of measurement methods.

[2] Standard method for the measurement of Pb, Cd, As and Ni in the PM_{10} fraction of suspended particulate matter.

Health risk assessment

Trace metal and BaP concentrations were used to characterise the distribution of cumulative cancer and non-cancer health risks in accordance with the USEPA (USEPA 2013) and CalEPA health risk assessment models (CalEPA 2003, 2008). All necessary health risk assessment model calculations are obtainable in the ESM. A detailed description of the USEPA and CalEPA models, and the general principles of model uncertainty, may be found elsewhere (Slezakova et al. 2011; Morello-Frosch et al. 2000; USEPA 2005; CalEPA 1996). Additional toxicity information and the parameters used for calculation in this study were obtained from the USEPA Integrated Risk Information System, Risk Assessment Information System and CalEPA chemical toxicity databases. According to USEPA, the incremental lifetime cancer risk (ILCR), or cancer risk (CR), determined by the CalEPA model represents an incremental probability of an individual developing cancer over their lifetime as a result of exposure to a carcinogenic compound. The cumulative cancer risk (CCR) posed to a receptor is the sum of the total risks from each individual exposure pathway (e.g. oral, dermal, inhalation, etc.) and/or might result from exposure to emissions from multiple species. Here, the CCR represents the sum of the ILCR (or CR) values obtained from exposure through inhalation to each of the five trace metals (As, Cd, Cr, Ni and Pb) and BaP. The acceptable baseline risk level is below 10^{-6}, whilst 10^{-4} is the upper limit of the range of acceptability. The CalEPA model was used in order to emphasise the increased sensitivity to carcinogens during early-in-life exposure and thus considers in detail different features: dose of air inhalation, age sensitivity factor, fraction of time spent at home and exposure duration for six age groups of the population (third trimester of pregnancy, $0 < 2$, $2 < 9$, $2 < 16$, $16 < 30$ and $30 < 70$ years). CR values were calculated and expressed for each age group and then summed to estimate the total cancer risk for the population aged 9, 30 and 70 years. Cumulative CR was obtained as the sum of the individual chemical total cancer risks for a 70-year exposure period and corresponds to the cumulative ILCR value obtained by the USEPA. All calculations were performed with the assumption that the bioavailability of trace metals and BaP in PM_{10} was 100 % (Diaz and Dominguez 2009).

Potential non-cancer effects of some chemicals were represented in terms of hazard quotient (HQ), which, for a single substance, is the ratio of the potential exposure to a substance (measured concentrations) and the level at which no adverse effects are expected (reference dose). An estimated HQ value above 1 indicates that, in this case, the concentration exceeds the threshold level and should be of public health concern (USEPA 2011b). When exposure involves more than one chemical and/or multiple exposure pathways, the sum of the individual HQs is represented as the hazard index (HI).

Transport analysis

The regional and long-range transport analyses of PM_{10}, As, Cr, Ni and Pb were performed by the use of 72-h air mass back trajectories and several models. The sampling site SL, located in the middle of the city centre at one of the largest squares and traffic junctions in Belgrade, and also with the highest number of concentration data, was chosen as a representative receptor site to investigate the influence of transport. The trajectories were dynamically calculated at half of the planetary boundary layer (PBL) height above the receptor site since the vertical profiles of pollutant concentrations remained relatively constant around that altitude (Stull 1988). Four trajectories, at 00, 06, 12 and 18 UTC, were calculated for each day using the HYSPLIT model (Draxler and Rolph 2014) and the 'opentraj' package (Opentraj 2015). The PBL height included in GDAS1 (GDAS 2015) was calculated for the receptor site using the MeteoInfo software (Wang 2014). Each trajectory that reached the ground level was excluded from the analysis (about 16 %). To differentiate between the loadings of transported and background pollution to the observed mass concentrations, a pronounced local contribution was excluded from the time series by the use of a frequency-differentiated nonlinear digital filtering algorithm implemented in the function baseline RollingBall (wm = 2, ws = 2) of the 'baseline' package (Kneen and Annegarn 1996) of the statistical software R, thus providing a baseline. Subsequently, trajectory sector analysis (TSA) was applied to the derived baseline in order to obtain the mean background levels and time series of transported pollution according to Stojić et al. (2015b, c). Furthermore, estimation of the potential non-local emission sources and their impacts on the observed concentrations of PM_{10} and constituents was performed using advanced TEMs including a potential source contribution function (PSCF), concentration weighted trajectory (CWT), residence time weighted concentration (RTWC) and the simplified quantitative transport bias analysis (sQTBA), all implemented in MetCor statistical software (MetCor v.1.0, revision 30; Rastogi 2013; Sofowote et al. 2015). All TEMs involve counting the frequency of back trajectory segment endpoints in grid cells that make up the geographical domain of interest for the receptor site. The main difference between the models is the method of incorporation of the measured concentrations within the trajectory endpoint frequency in each grid cell. PSCF shows the percentage frequency of trajectory segment endpoints above a concentration threshold relative to the total trajectory segment endpoints in each grid cell. In CWT, every concentration is used as a weighting factor for the residence times of all trajectories in each grid cell and then is divided by the cumulative residence time from all trajectories. RTWC applies a similar concept; however, the concentrations are equally divided along each trajectory initially and then the logarithm of the redistributed concentrations is used as a

weighting factor. The model sQTBA uses Gaussian distributions to calculate the natural transport potential function of a substance based on the distance and time interval away from the receptor (Watson et al. 2008). Visualisation of the TEM outputs and health risk results used the 'raster' and 'rasterVis' (Hijmans et al. 2015) packages from the statistical software R.

Results and discussion

Statistical analysis

The basic statistical parameters and average annual concentrations of PM_{10}, PM_{10}-bound trace metals and BaP are presented in ESM Tables S-2a and S-2b, respectively. The annual average PM_{10} concentrations were 32.49–80.62 $\mu g\ m^{-3}$, with the lowest values in the inhabited parts of suburban and rural areas and the highest concentrations observed at the sites affected by industrial pollution and intensive traffic. The seasonal variability of the concentrations (ESM Fig. S-1a–o) could be the consequence of specific meteorological conditions (Rost et al. 2009) and the intensification of anthropogenic pollution sources during the colder part of the year. A bimodal type of PDF characterises winter, indicating the existence of more than one dominant source, especially in areas where individual heating installations are in use. Trend analysis (ESM Fig. S-2a, b) generally showed a temporal decrease of the PM_{10} concentration in the Belgrade area. At two sampling sites of different type (VC affected by industrial pollution and FVM close to highway E75), PM_{10} reduction was noticeable (about 11 % or 7 $\mu g\ m^{-3}$ for the entire period). A significant increase of the concentration level of 4.5 % (1.4 $\mu g\ m^{-3}$) for the entire period was observed at sampling site KBC.

The average concentrations of PM_{10}-bound Mn, Ni, Cd and Pb were generally lower compared to other European cities, whilst the concentrations of As and Cr were higher (EEA 2015; Murillo et al. 2013; Querol et al. 2009). Arsenic concentrations were above the lower assessment threshold (2.4 $ng\ m^{-3}$: EU 2004) at almost all stations. The target value (6 $ng\ m^{-3}$) was exceeded at sampling sites LA and VC during every year of the analysed period, with the maximum annual averages for 2013 as 29.4 and 16.5 $ng\ m^{-3}$, respectively. The shape of the PDF of As (Fig. 2 and ESM Fig. S-1a–n) and its strong seasonal dependency suggest the existence of more intensive emission sources during the heating season, particularly in densely inhabited areas.

Areas affected by lignite coal mining and combustion processes are characterised by high values of As in ambient air, as previously evidenced by Todorović et al. (2015). This metal in coal occurs in the form of both organic and inorganic compounds and can be totally volatilised during combustion (WHO 2001). Thus, coal burning might be one of the most important emission sources of arsenic during winter in this region. The decreasing trend over the years in urban areas could be induced by the implementation of remote heating systems in the city itself, but increasing trends are still present in rural industrial parts.

The chromium concentrations averaged for the considered period were 7.05–24.65 $ng\ m^{-3}$, with the highest values at traffic-exposed locations. Trend analysis indicated a significant increase at all sampling sites (ESM Fig. S-2a–h), with a growth rate of up to 9.26 $ng\ m^{-3}$ (260 %) for the entire period at sampling site LA. The growth trend of chromium concentrations, in contrast to the descending PM_{10} trend, indicates a change in the composition of PM_{10} during the examined period. Unlike the other species, Cr showed higher concentrations mostly during the warm part of the year (ESM Fig. S-1a–o). In spring, the observed values of Cr were more concentrated in the middle of the distribution than in the tails (bell-shaped PDF curve), assuming a considerably strong homogeneous distribution of Cr in PM_{10}, which was much less affected by significant human activities. This result can also be inferred as a consequence of the fairly convincing crustal emissions (Pongpiachan and Iijima 2016). The absence of rainfall during summer caused increased resuspension of dust, which may contain chromium compounds, whilst the multi-modal probability distribution of Cr concentration indicates the existence of more sources of different types and intensities.

At four sampling sites affected by traffic pollution (BAS, FVM, KBC and JNA), the observed Ni concentrations exceeded the limit value of 20 $ng\ m^{-3}$ (ESM Table S-2b). High Ni concentrations characterise each mode of transportation due to the high level of Ni in diesel, petrol and fuel additives and also may be released through the engine exhaust due to wear and tear of the engine (Menzie et al. 2009). Close to highway E75, an increase of Ni concentration was observed at the rate of 2.66 $ng\ m^{-3}$ (15 %) for the entire period, but the most important growth trend was noted at two sampling sites away from the city centre (KR and RS). At these sites, located in residential areas, the average Ni concentrations for the analysed period were 7.11 and 9.04 $ng\ m^{-3}$, respectively, but the increasing trends of 62 and 72 % for the entire period may be an indicator of reinforcing the existing or forming additional sources of nickel in this area. At urban locations BAS and JNA, analyses showed decreasing trends, which resulted in a decrease of Ni concentrations below the limit value in 2015.

The PDF for Mn during each season indicated the contribution of dissimilar emission sources and higher concentrations during the spring and summer. The highest Mn concentrations were observed in the proximity of the central bus station (BAS, 68.22 $ng\ m^{-3}$) and near the foundry complex (RF, 65.19 $ng\ m^{-3}$), where the increasing trend during recent years was very high (293 %). Concerning anthropogenic activities, almost 80 % of the industrial emissions of manganese are attributable to iron and steel production facilities, whilst power plant and coke oven emissions contribute about 20 %
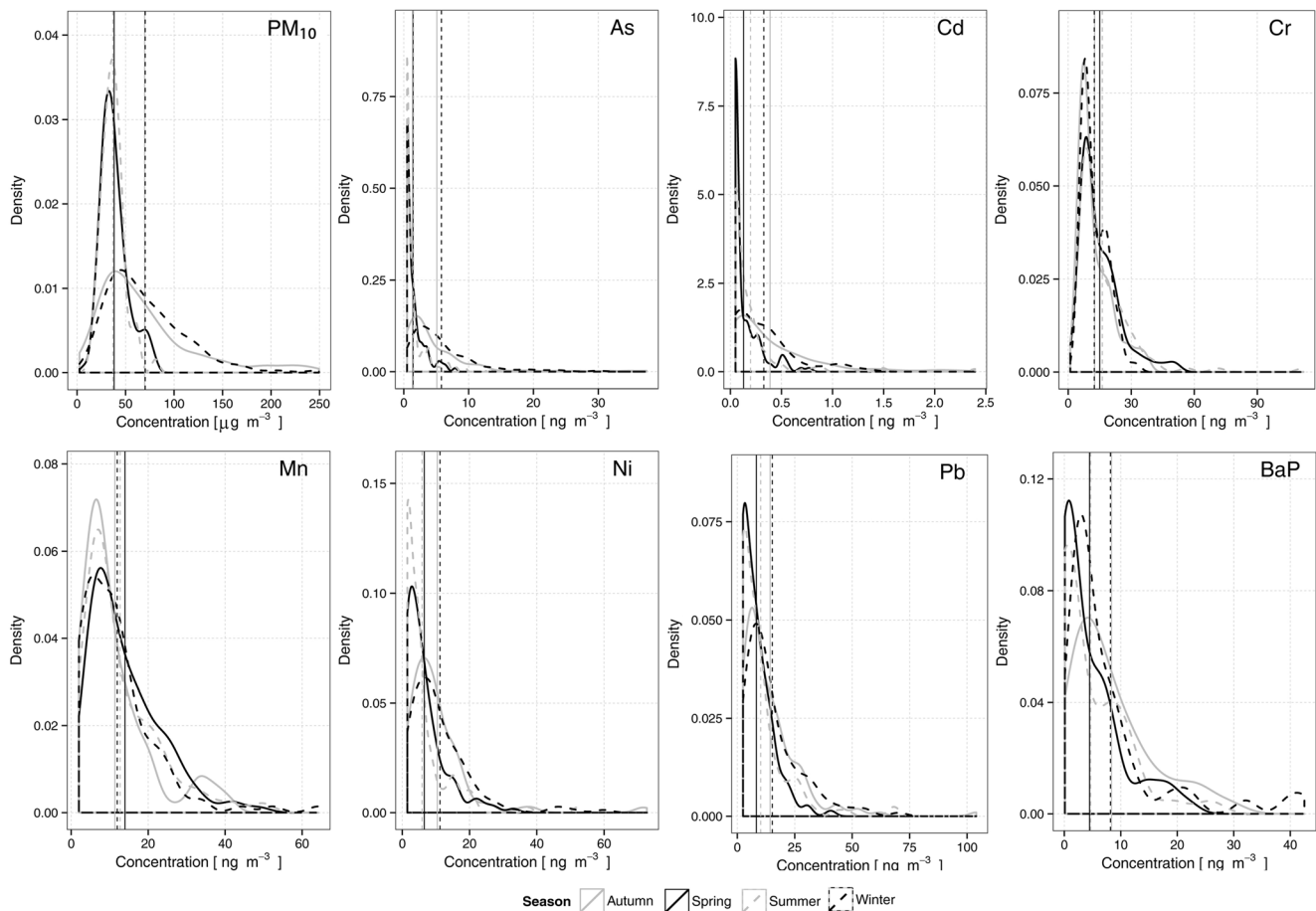
Fig. 2 Probability distribution of PM_{10}, As, Cd and Cr (*above*) and Mn, Ni, Pb and BaP (*below*) concentrations measured at sampling site SL

(ATSDR 2012). Also, close to the foundry (RF), the average Pb concentrations were the highest in the examined area (89.41 ng m^{-3}), with a positive growth rate of 9 %. At the other sites, Pb levels were significantly lower, much below the limit values (500 ng m^{-3}), because lead usage as a gasoline additive was prohibited in 2011. According to the PDF, the high Cd levels characterised winter, suggesting the impacts of fossil fuel burning and increased traffic intensity during this colder part of the year.

Due to exceeding the limit value (1 ng m^{-3}, Directive 2004/107/EC) at all sampling sites, BaP remains one of the main concerns in the area. According to the results of the random forest model (ESM Table S-3), BaP was also the most important measured variable predicting PM_{10} mass concentrations at almost all sampling sites, followed by As at some urban locations. The highest annual average BaP concentration (56.84 ng m^{-3} in 2015) with an increasing trend of 42 % was observed in the area near to the coal mine and thermal power plant (LA). At the other locations, the annual average concentrations were in the range 0.75–12.39 ng m^{-3}, with a significant decreasing trend in the city centre as a result of transferring to the remote heating system. The PDF of BaP shows a very strong seasonal variability, with distribution

shifting to higher concentration levels and more than ten times higher mean concentrations through the colder part of the year.

Health risk assessment

The results of the health risk assessment, CCR and HI values calculated according the USEPA and CalEPA models in the wide Belgrade area and urban part of the city, are presented in Fig. 3 and ESM Tables S-4a and S-4b.

Based on the average As concentrations for the whole analysed period, the ILCR values were higher than 10^{-5} in the surroundings of the industrial complexes. Toxic non-cancer health effects were significant too, with an HQ index value of 1.23 (ESM Tables S-4a and S-4b). The oxidation state of chromium in the compounds, present in ambient air, determines the toxicity of these compounds. Hexavalent chromium (Cr(VI)), mainly originating from anthropogenic sources, is the only form that is considered as highly carcinogenic. There is no information provided regarding the chromium oxidation state, and in this case, it is usual to generate 'default' speciation profiles. Mancuso (1997), forming the basis for the estimation of cancer potency for Cr compounds, suggests that
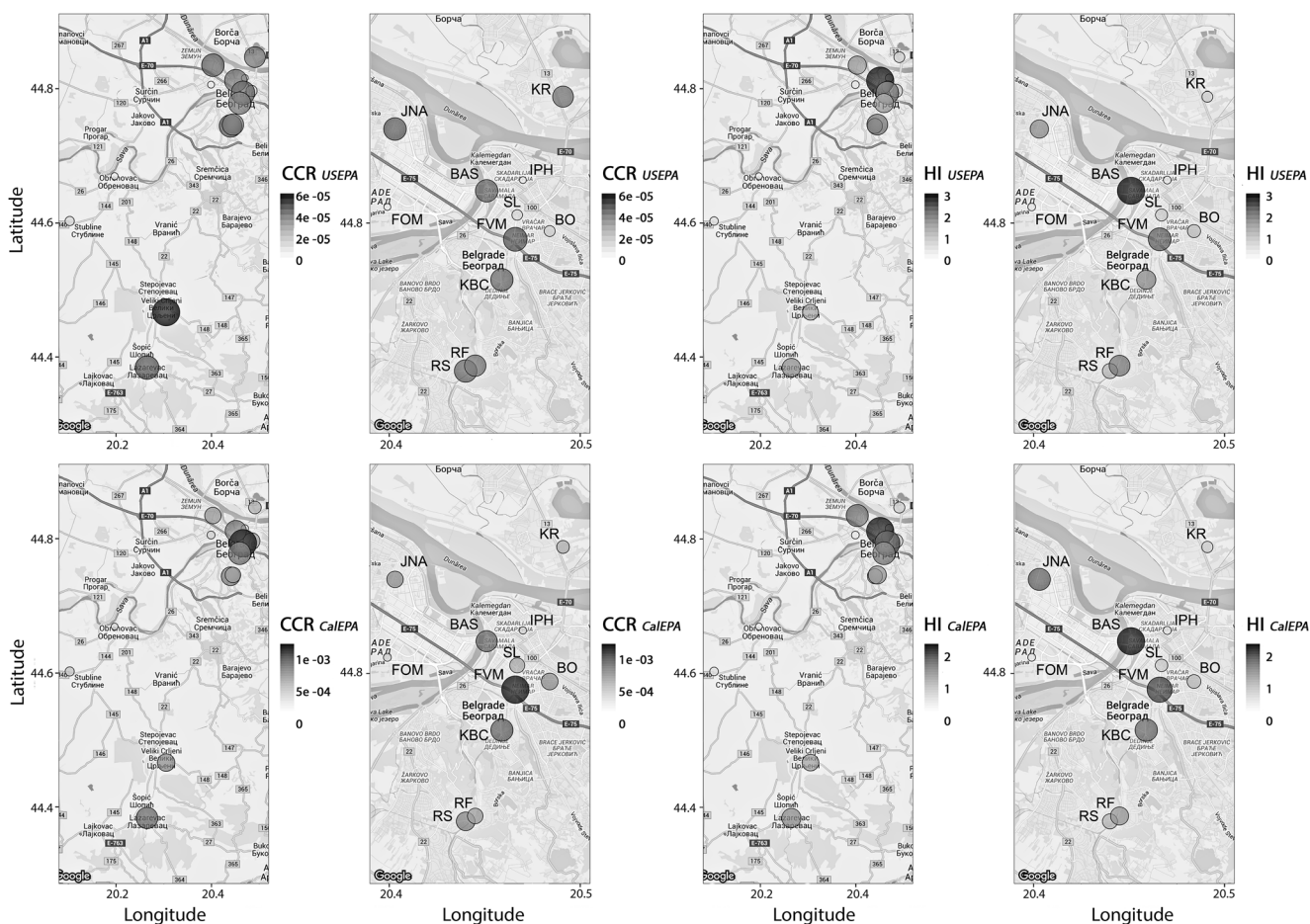
Fig. 3 Cumulative cancer health risk (*CCR*) and hazard index (*HI*) according to the USEPA (*above*) and CalEPA (*below*) models for the Belgrade area and urban city centre

in an urban area, one-seventh of the total chromium concentrations is hexavalent (Cr(VI)). According to this proposal, only one-seventh of the measured Cr concentrations was used for the calculation of ILCR/CR values. Additionally, CalEPA, as a health protective assumption, recommends a high value of cancer potency factor for Cr(VI), which causes higher CR values compared to ILCR. ILCR was in the range from 4.97×10^{-6} to 1.74×10^{-5} at the sampling site located near the road, whilst CR values were above the acceptable risk level for each age group in the wide Belgrade area (ESM Tables S-4a and S-4b). Bearing in mind the increasing trend of concentrations in the examined area, the cancer health risk will exceed the acceptable level according to both models in the next 2 years. The ILCR and CR for Ni, Cd and Pb compounds were in the acceptable range, with the highest values in the urban area. Even with the highest concentrations observed during the winter months, the risk was acceptable both for the population of children and adults. For Mn and Ni compounds, the estimated non-cancer effects were significant, with the highest HQ values (above 1) at traffic-exposed sampling sites. In the industrial areas, the ILCR value for BaP was 1.19×10^{-5}, whilst according to the CalEPA model, CR was

above the acceptable level (8.98×10^{-4}), with the highest estimated risk for the most sensitive age groups ($0 < 2$ and $2 < 16$ years old). Regarding the seasonal average concentrations of BaP, the cancer health risk calculated for spring and summer, the seasons with the lowest concentrations, was within the acceptable level.

Based on the concentrations of five trace metals (As, Cd, Cr, Ni and Pb) and BaP, the CCR approached the acceptable level (10^{-6}) according to the USEPA, whilst regarding the CalEPA model, the values were higher than 10^{-4}. The highest CCR values were noted not only in urban areas in the city centre but also in the suburban industrial area near to the coal mine (Fig. 3). Chromium and arsenic with different shares were major contributors to CCR. Portions of Cr compounds were higher in the urban city centre with intensive traffic, whilst As was dominant in industrial areas (70 %). The portion of BaP in CCR was about 10 % at all sampling sites, whilst Pb had the largest influence (3 %) in the vicinity of the foundry (RF). Ni and Cd had no significant contribution to the obtained CCR.

The toxic non-cancer impact on human health of the five trace metals (As, Cd, Cr, Mn and Ni) at traffic-exposed

locations can be represented in the following order HQNi > HQCr > HQAs > HQMn > HQCd, whilst at the places with industrial facilities, the largest contribution arises from arsenic compounds. HI values were higher than 1 at ten sampling sites, suggesting significant toxic effects (ESM Tables S-4a and S-4b).

Transport analysis

Besides strong and dominant proximate sources, the concentrations of some compounds may be noticeably influenced by transported pollution from remote sources. The PDF of PM_{10} and some of the analysed trace metals indicates the contribution of more than one source during each season (ESM Fig. S-1a–o). According to the TSA, at sampling site SL, Cd and As mainly originated from local sources, whilst the highest background levels were observed for Mn and Cr (Table 1). Consequently, the shares of transported pollution amounted from 8.95 % in Mn to 36.07 % in As concentrations. Also, very high background levels were observed for PM_{10} (55 %), whilst about 16 % of concentrations were transported to this area during the analysis period. Bearing in mind the amount of transported pollution (>10 %), TEMs were applied in order to resolve potential distant sources of PM_{10}, As, Cr, Ni and Pb. Cd was excluded from this analysis due to low concentrations, whilst BaP was not considered because of an insufficient number of data.

The results of TEM applied on PM_{10} concentrations showed that the area was influenced by strong regional sources located in the E and S–SW (PSCF) and distant sources in the E–NE regions (CWT, RTWC and sQTBA; Fig. 4). Regarding the As compounds, the results of the PSCF and CWT models indicate the influence of polluted air masses from the W, E and SE areas, whilst RTWC specified potentially the most important sources being located in Germany, Poland, Croatia and Ukraine. Both PSCF and CWT suggest a potential origin of chromium compounds in Eastern European countries and the area surrounding the Black Sea. RTWC highlights strong sources in West Europe and also in eastern areas, whilst sQTBA estimates the largest importance of regional and proximate sources. Ni compounds may be transported from the E and SW regions, with the exception of the sQTBA model, which suggests very distant sources in North Europe. In the case of Pb compounds, the source areas identified by PSCF and CWT are located in neighbouring countries; model RTWC emphasised strong sources in Denmark, Poland, Romania and Bulgaria, whilst sQTBA indicated the dominant influence of nearby sources (ESM Fig. S-3a–d).

Conclusion

The levels of ambient PM_{10} and PM_{10}-bound metals (As, Cd, Cr, Mn, Ni and Pb) and BaP concentrations, and the potential adverse inhalation health outcomes, were observed in a large urban area. Different analytical methods, including basic statistical, probability density function, random forest and trend analysis, were complemented by the USEPA and CalEPA models of health risk assessment and an improved transport analysis based on trajectory sector analyses and trajectory ensemble models. The highest average PM_{10} concentrations were obtained at the places affected by industrial pollution and intensive traffic. Arsenic, chromium and BaP had the largest impact on the air quality and population cancer health risk. With the highest values for CCR, areas affected by coal mining and combustion processes could represent the most endangered zones. Within these locations, even with the lowest As concentrations, during summer, the ILCR values remained over 10^{-5}. The average BaP concentrations in the surroundings of industrial activities have to be reduced more than tenfold in order to approach the acceptable range of cancer health risk. Toxic, non-cancer health risks were highest for As, Ni and Cr compounds. The maximum hazard indices were estimated for urban locations, indicating the threat of traffic pollution. Along with pronounced local contribution, the results of the trajectory sector analyses estimated the contributions of potential remote emission sources of different species in the range of 8.95–36.07 %. Transport pathways associated

Table 1 Contribution of transport, background and local production to the measured concentrations of PM_{10}, As, Cd, Mn, Ni and Pb at sampling site SL during the period 2011–2015

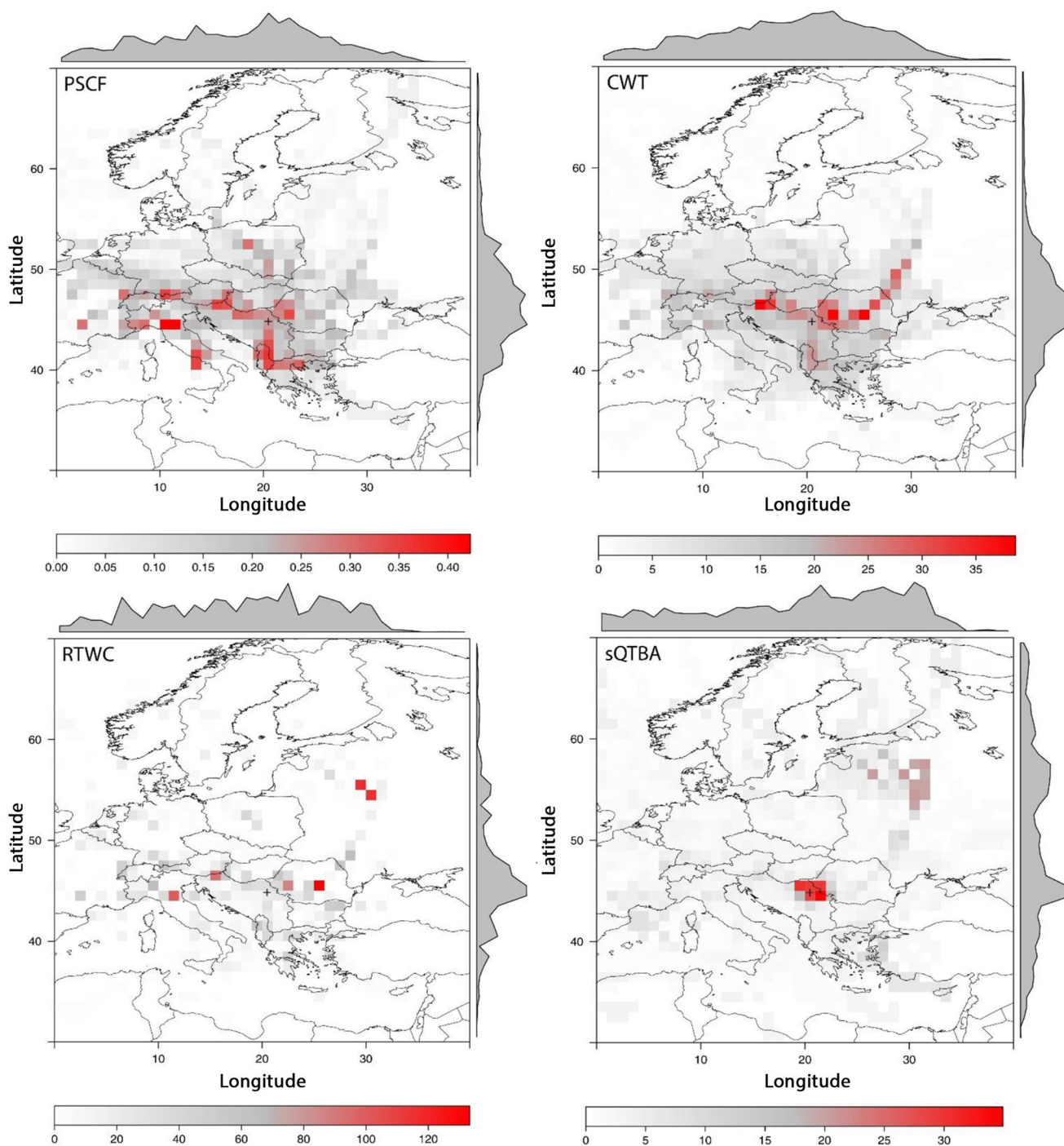|	PM_{10} ($\mu g\ m^{-3}$)	As (ng m^{-3})	Cd (ng m^{-3})	Cr (ng m^{-3})	Mn (ng m^{-3})	Ni (ng m^{-3})	Pb (ng m^{-3})
Mean	54.02	3.48	0.26	14.06	12.46	8.52	12.04
Transported	8.71	1.25	0.05	2.28	1.11	1.72	2.26
Transported (%)	16.12	36.07	20.62	16.24	8.95	20.16	18.77
Background	30.05	0.52	0.06	8.66	7.11	3.18	4.40
Background (%)	55.61	14.89	22.84	61.61	57.04	37.28	36.52
Local production	15.27	1.70	0.15	3.11	4.24	3.63	5.39
Local production (%)	28.26	49.04	56.54	22.15	34.01	42.56	44.71

Fig. 4 Potential sources of PM_{10} resolved using the PSCF (probability), CWT, TRCW and sQTBA (in micrograms per cubic metre) models at sampling site SL during the period 2011–2015

mainly with eastern air masses appeared to have a significant impact on the air quality of the Belgrade area. In the forthcoming period, control of biomass burning, due to a transfer to the distant heating system in the city centre, and implementations of new technologies in the industrial sector might be principal objectives in mitigating the air quality and population health risk in the study area. Furthermore, since the long-range transport significantly

contributes to PM_{10} and some trace metal concentrations, global action must accompany local and national efforts to reduce pollution emissions and their effects on human health.

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