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Benzo[a]pyrene toxicity equivalent level and lifetime lung cancer risk in Belgrade area, Serbia

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- Air quality continues to be a very important issue for public health and the environment

- Particulate matter (PM) and ozone (O3) pollution are particularly associated with serious health risks matter and ozone (EEA, 2013)

- Among the chemical species bonded on PM surfaces polycyclic aromatic hydrocarbons (PAHs) are of major significance

- According to some studies a 10 $\mu g/m^3$ increase in PM_{10} concentration can be yield 1% increase in overall mortality (Lipmann, 1998)

- Major sources of PAHs, especially in urbanized areas, are gasoline and diesel vehicles, coal and wood combustion and industrial processes (Mostert et al., 2010; Tobiszewski et al., 2012)

- For each sources such as: diesel and gasoline combustion, crude oil processing products and biomass burning (Ravindra et al., 2008; Yunker et al., 2002), the PAH emission profile is different

- PAH diagnostic ratios also as source apportionment techniques can be used to identify some potential emission sources (Teixeira et al., 2012; Tobiszewski et al., 2012,Park et al., 2011; Jang et al., 2013)

- B[a]P is used as an indicator of human exposure to PAHs

- In order to estimate the health risks for humans the benzo(a)pyrene-equivalent (BaP eq) was evaluated by multiplying the concentrations of each PAH with their toxic equivalent factors (TEF) (Akyüz at al., 2008).

- Toxic effect of some PAH is stronger, even at much lower concentrations, due to its high TEF, which have been reported by many researches (Knafla et al., 2006)

- The toxicity of other PAHs is converted into toxicity equivalency factors (TEFs) according to B[a]P to evaluate their relative toxicities

- The assessment of lifetime lung cancer risk due to exposure to PAHs was calculated according to the formula:

  Lifetime lung cancer risk = B[a]P Peq x UR,
  where UR is inhalation unit risk of exposure to B[a]P .

- In this study, the UR is $8,7x10^{-5}$ per ng/m^3 was taken according to World Health Organization (WHO, 2000).

- In Serbia, monitoring of PM less than 10 μm (PM_{10}) started from 2003 at three stations in Belgrade within the Local monitoring network run by the Institute of Public Health of Belgrade.

- Today in the Belgrade Metropolitan region in framework of Local and State Air Quality Monitoring Networks there are running 15 automatic monitoring stations, 11 of them in the city center and 4 nearby two power plants

- In Belgrade the first data on the PAH composition of PM_{10} and smaller fractions, $PM_{2.5}$ and PM_1 started within the framework of the WeBIOPATR project (2006-2009)

- In this paper we determine levels and the total carcinogenic activities (total BaPeq concentrations) for PAH in PM_{10} collected within local monitoring network of Public Health of Belgrade (IPHB)

- Sampling was done during heating and non-heating season in period 2010-2013 at different sampling sites:
  - urban - traffic (UT), located in strong city centre (IPHB, Slavija-SLA)
  - urban - traffic and residential heating (UT+H), boundary of central zone (Vračar-VRA)
  - rural industrial and residential heating (RI+H) (Grabovac-GRA, Obrenovac-OBR)
  - suburban industrial (SI) (Lazarevac-LAZ)

Sampling sites

- Lazarevac-LAZ, proximity and influence of coal mine facilities and coal-fired thermal power plant "Kolubara A", open pit mining of coal and other facilities of the Kolubara mining-industrial complex are in the vicinity

- It is industrial sampling site, suited in the one of Belgrade's municipalities, located 40 km south-west from the inner zone and 10 km east from Kolubara mining-industrial complex

- Sampling site is located in the suburban area in the vicinity of local roads and regional E-763 road. Sources of air pollution in the Kolubara mining-industrial complex, located 60 km south of Belgrade inner zone, are the lignite open pit mine spanning over 130 km^2 ; thermal power plants, coal heating plants and the coal processing plant "Kolubara" (www.tent.rs/en).

❖ Grabovac, GRA -coal-fired thermal power plants "TENT A", "TENT B" and other facilities around such as ash and coal landfills. It is also primary industrial sampling site located beside a local road in the rural zone, lying about 15 km to the south-west of Belgrade inner city zone and 15 km far from town of Obrenovac and the coal-fired thermal power plants TENT A and TENT B (www.tent.rs/en/). Sampling site is located 3-4 km from the ash and coal landfills.

❖ Obrenovac, OBR is sampling site with influence of industry. Obrenovac is situated 30 km south-west of central Belgrade near bends of the river Sava to the north. The river Kolubara flows to the east of the town on its way to join the Sava. Largest Serbian thermal power plant Nikola Tesla is located on the outskirts of the town. By far the largest one in Serbia these power plants use lignite[i] mined from the RB Kolubara as fuel. Coal is transported from the mines via a normal gauge railroadabout 30 km long capable of supplying a total of 37 million tons of coal a year.

❖ Slavija, SLA-24h frequent traffic roundabout intersection called Slavija, site located in the inner city center of Belgrade. It is a traffic sampling site in the center of Belgrade with high traffic density. Slavija is well known as one of the most frequent traffic roundabout intersection junction in Belgrade.

❖ Vračar, VRA is traffic/heating sampling site. It is located in the urban area in Belgrade, in the center of town, with high traffic density. Although during last 10 years there was a fire over 1000 boiler which used liquid (fuel oil and diesel) and solid (coal) fossil fuels and their replacement district heating system there are many individual domestic heating in this area. Their influence on air pollutions is significant during the winter season.

❖ Institute of Public Health of Belgrade, IPHB- traffic sampling site is located in Bulevar despota Stefana 54a in the old part of town. The location of Institute is specific because it is a canyon type of street with high traffic jam which is very slow. In this area there are individual domestic heating also but not so much as in the VRA area.

Methods

- PM_{10} aerosol fractions were sampled during 2010 and 2013:
  - during 2010-2011: GRA, SLA, LAZ (133,148,163 samples, respectively)
  - during 2012-2013: VRA, IPHB, OBR (92, 129, 129 samples, respectively)

- All PM_{10} samples were collected by European reference low-volume sampler (Sven/Leckel LVS3 with flow rates 2·3 m^3 h^{-1}) provided with inlets to collect particulate matter onto 47 mm Whatman filters·

- Samples were collected on a daily basis (24 hours) with one 'field blank' per week (EEC, 1999)

- Gravimetric measurements were conducted according to EN 12341 for PM_{10} (CEN, 1998)

Collected samples were prepared according to Compendium Method TO-13A (US EPA, 1999) using Gas Chromatography with Mass Selective Detector

- PAHs were extracted in a microwave with mixture of solvents hexane: acetone (12·5 ml n-hexane: 12·5 ml acetone) according to EPA 3546·

- All samples were analyzed by GC Agilent 6890 N with Mass Selective Detector Agilent 5973 MSD· Capillary column DB-5 MS (30 m x 0·25 mm x 25 µm) was used

- As external standard for calibration curve we used Ultra Scientific PAH Mixture PM-831, which consists of 16 compounds, each of 500·8 ± 2·5 µg/ml concentration

- Method Quantification Limit (MQL) for all PAHs was 0·02 ng /m^3

- As internal standard, we used Ultra Scientific Semi-Volatiles Internal Standard Mixture ISM-560 with deuterated compounds

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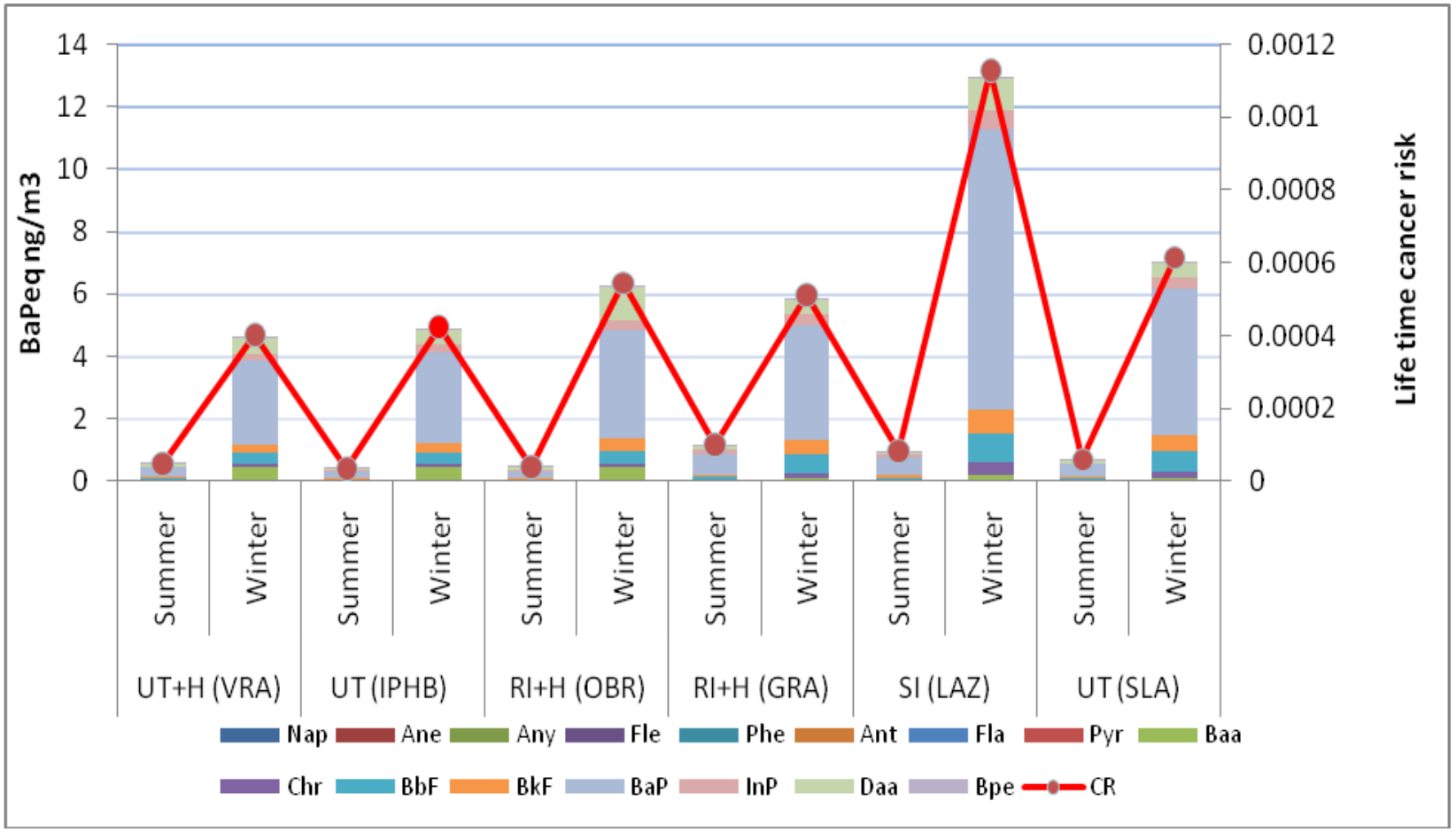
RESULTS

- The percentage of B[a]P to total PAHs was from 7-11 % on all sampling sites in the whole sampling period with number of values exceeding target value of 1 ng/m3. According to the Annual report of the European Environment Agency for 2010 (EEA, 2012) average annual concentration of B[a]P exceeded the target value in six countries (Austria, Bulgaria, the Czech Republic, Hungary, Poland and Slovakia).

- The highest content of B[a]P in total PAHs was at site OBR (RI) in winter (11.72 %) and the lowest was at site LAZ (SI) in summer (7.09 %).



Plot of BaPeq (ng/m^3) and lifetime cancer risk of each sampling site

- The total carcinogenic activities (total BaPeq concentrations) for collected PM_{10} during the winter season were found to be between 4,60 and 12,96 ng/m^3, highest at the LAZ site

- During the summer season BaPeq were between 0,39 and 1,14 ng/m^3, lowest at the SLA site and highest at GRA.

- During both seasons, BaPeq were similar at SLA and GRA and about two times as high at LAZ sampling site.

- In Zonguldak, Turkey PAHs BaPeq were 1,20 in $PM_{2.5-10}$ in winter and 0,27 in summer (Akyüz at al., 2008).

- Mean values of BaPeq concentrations for the whole sampling period (summer and winter season) were in Athens, 1,6 ng/m^3 (Marino et al., 2000); in Argel, 3,4 ng/m^3 (Yassaa, 2001) and in an urban area in Florence with abundant traffic, 2,6 ng/m^3 (Lodovici et al., 2003).

- The ambient concentration of 16 PAH and their toxic equivalent were used to calculated lifetime cancer risk. It was also plotted the estimated lifetime cancer risk from PAH in the atmosphere

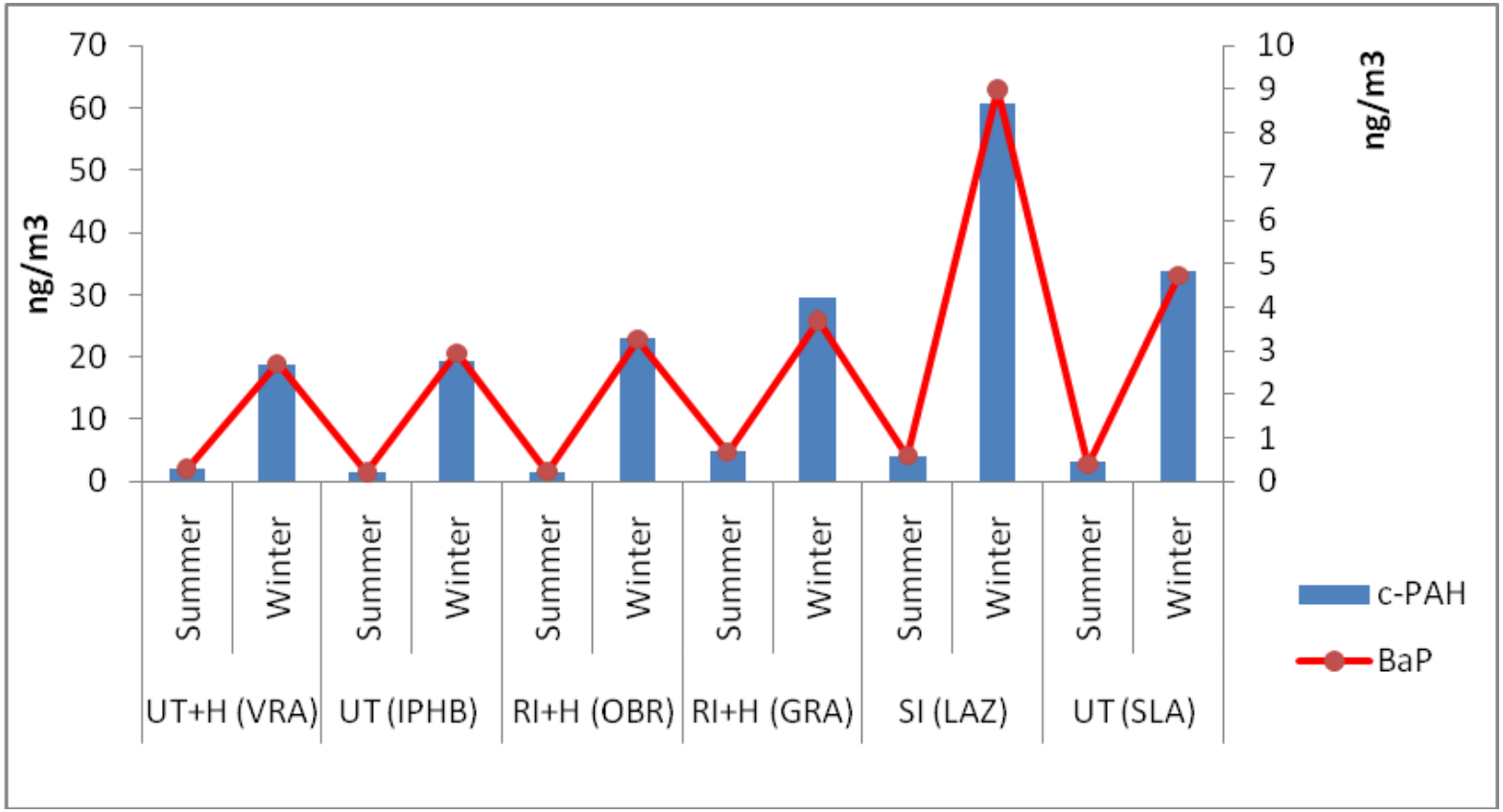
- All values for the lifetime cancer risk were above target individual lifetime risk, which is 10^{-6} (US EPA, 2012)

- The highest risk and the most negative impact on human health (the highest lifetime cancer risk concentrations) was found at the LAZ site due to strong impact from the Kolubara mining-industrial complex, consisting of coal mine, thermal power plant and other facilities

- c-PAH :
- B[a]P-Group 1
- benz[a]anthracene-Group·2A
- chrysene,benzo[b]fluoranthene,benzo[k]fluoranthene,dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene-Group 2B

- The concentration of total c PAHwas the highest in winter at LAZ (60,82 ng/m^3) almost twice than SLA (33,6 ng/m^3) and GRA (29,60 ng/m^3)

- The concentration of B[a]P was have shown the same trend: the highest at LAZ in winter (8,99 ng/m^3), than SLA (4,72 ng/m^3, GRA 3,70 ng/m^3



Concentration of c-PAH and BaP

- During the summer concentration of total c-PAH was the highest at GRA (4·94 ng/m^3), than LAZ (4·14 ng/m^3) and SLA (3·27 ng/m^3)

- The same trend was for B[a]P

- Remaining c-PAH showed the different trend in summer - this impact is could be even more negative over the most sensitive population, children and older people, in particular during winter season·

CONCLUSION

- The highest BaPeq level were found at rural industrial site during the heating season and the lowest at urban traffic site in non-heating season

- The carcinogenic risks for humans are much higher at all sites during heating than in non-heating season

- The relative contribution of each PAH to the BaPeq levels shown that B[a]P and DahA dominated the BaPeq levels

- All values for the lifetime cancer risk were above target individual lifetime risk, which is 10^{-6}