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URBAN BENZO(A)PYRENE CONCENTRATIONS IN AIR: A MODELLING STUDY AND VALIDATION

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Abstract: Benzo(a)pyrene (BaP), a carcinogenic organic compound originating mostly from incomplete burning of organic matter, is studied in the air of Tartu, second largest town of Estonia (approximately 100000 inhabitants). According to the episodic filter measurements made by the Estonian Environment Research Centre (EERC), almost 1000 daily averages in total since 2013, it appears that the European target value (1 ng m^{-3} absorbed in PM_{10} fraction) is likely exceeded by factor up to 2 in dwelling areas, where the local wood heating prevails. The inventory of heater and stove emissions, based on laboratory measurements of the ratio of BaP, particulate matter in emission gases and estimated emissions of PM_{10} shows that domestic heating is highly prevailing over street transport and communal heat production. The modelling study with Gaussian plume model AEROPOL indicates fair agreement with measured values: the average modelled and measured concentrations during 2017 in the permanent monitoring station (292 daily measurements, situated close to the heating emission area) agree with precision of 5%, whereas the linear correlation coefficient is +0.79. The modelled yearly average concentration in hotspot is 2.2 ng m^{-3}. In years 2013 – 2016 (less measurements) the correlation coefficients range from 0.47 to 0.67 and disagreement between modelled and measured values is up to 50%, both over- and underestimated annual averages occur. Measured BaP is rather well correlated (+0.67) with carbon monoxide, another product of incomplete burning. Correlation with $PM_{2.5}$ is remarkably lower (+0.46). The multi-linear regression of BaP concentration shows statistically significant dependence on CO (positive) and NO (negative), leaving out SO_2, NO_2 and also narrowly PM_{10}, as statistically insignificant at 95% confidence level. In multi-linear regression with meteorological parameters the negative dependences on air temperature and wind speed are found. This result is obviously related to the emissions mostly in heating season (September to May) and the effect of wind, dispersing the local emissions. The measures to reduce the concentration of BaP in future are discussed.

Key words: *Benzo(a)pyrene, urban air, pollution, residential heating, modelling.*

INTRODUCTION

Benzo(a)pyrene (BaP) is one of polycyclic aromatic hydrocarbons (PAH) occurring in ambient air in composition of particulate matter. BaP is known as a carcinogenic compound originating mostly from incomplete burning of organic matter, e.g. in combustion of solid and liquid fuels (Gianelle et al., 2013) and cooking (Aygün & Kabadayi, 2005; Lee & Shim, 2005).

Since the beginning of 21st century the measurement equipment has gradually become sufficiently sensitive to detect BaP in ambient air by routine air quality monitoring equipment. Assessing the BaP pollution levels in European Union (EU), it was found that about 20% of the population in EU is exposed to higher concentrations than the European target value 1 ngm^{-3} (annual average) and only 7% live in areas where the concentration is lower than estimated acceptable risk level 0.12 ngm^{-3} based on data from 2012 (Guerreiro et al., 2016). However, large uncertainties remain, as only 60% of population was covered with sufficient monitoring network.

It was found that the concentrations of BaP are highest in certain parts of Central Eastern Europe, Poland and Romania in particular, where residential heating, which is based on wood and coal, is prevailing. In general, residential heating is prevailing with 82% of BaP emissions in EU as whole, followed by various industrial processes (11%), natural emissions including forest fires, and road transport (both less than 3%). Share of electricity and communal heat production is less than 1% of total emission (Guerreiro, 2015). Most of the territory of Estonia was not covered with reliable data, however, concentration exceeding the threshold level, was reported for Tartu, the second largest town of Estonia (about one hundred thousand inhabitants).

This paper is about monitoring of BaP in air (PM_{10} fraction) performed in Tartu by Estonian Environmental Research Centre (EERC) since 2013 and atmospheric dispersion modelling to identify the sources, validation of model application against air quality monitoring results and future projections to reduce the pollution level. Correlations of BaP with routinely monitored pollutants ($PM_{2.5}$, NO_X, CO, SO_2) and weather parameters are considered to understand its formation mechanisms and find proxies easier to detect.

METHODS AND MODELS

Ambient air pollution monitoring

In an air quality monitoring station based in Tartu, Southern Karlova site (58º22'14" N, 26º44'5" E), close to areas of intense residential heating (multi-flat houses built in late 19th and early 20th century), PM_{10}, $PM_{2.5}$, NO_X, CO, SO_2 are routinely monitored on hourly basis. In addition, the daily average concentrations of BaP in PM_{10} fraction were measured during 2013 – 2017 with variable frequency from the filters used to collect the samples of $PM_{10.}$ BaP was analysed from the gas and particle phase from the PM_{10} high-volume sampler filters and from PUF (Polyurethane Foam) according to ISO 12884 using mass-spectrometer.In total 544 daily averages were measured in the monitoring station. Measurements in two temporary monitoring sites based in northern part of Karlova (174 daily averages) and in Tamme area with prevailing private houses (214 daily averages) were performed in addition.

The Pearson correlations and multiple regression analysis were used to investigate the relations of BaP with other pollutants and weather parameters. To understand the dependence of BaP daily average concentrations on wind direction, the days were classified in respect to prevailing wind direction of four: north, east, south, west.

Air pollution dispersion modelling

Applied AEROPOL model (Kaasik & Kimmel, 2003, Geertsema & Kaasik, 2019) is based on Gaussian plume concept, with considering the partial reflection of the plume from underlying surface and extensively used and validated in urban dispersion studies before (e.g. Carlsen et al., 2017, Kaasik et al., 2019). The emission data are based on geo-related inventory of emissions from locally heated residential houses by EERC (Maasikmets, 2019), where the emissions are approximated using the national building register data, assuming energy consumption 242 kWh per year per m^2 of house area. The laboratory measurements performed by EERC give emission rate 0,195 $mgMJ^{-1}$ of BaP and 276 $mgMJ^{-1}$ of particulate matter as average of typical masonry heaters and stoves in use in Estonia and typical firewood of variable moisture

(Teinemaa et al., 2013). The monthly emission coefficients were applied, assuming that no heating is occurring at monthly average temperatures above 15 °C and at lower temperatures the emission is proportional to difference between 15 °C and ambient temperature. Three main boiler houses and the main traffic streets (based on traffic counting data and emission coefficients by Gianelle et al., 2013) within the city were taken into account as well.

The model runs were performed for densely populated area of Tartu, dimensions 9 by 8 km, with output grid resolution of 50 m. To optimize the computation time, the emission sources of individual houses were aggregated to 0.25 km^2 square sources. The concentrations were modelled on annual basis with 4-hour time resolution. Apart of annual average concentrations, the time series from locations of above-mentioned monitoring sites were extracted. The publically available weather observation data from Tartu-Tõravere station (at distance about 20 km) of National Weather Service of Estonia were used as meteorological input for modelling.

RESULTS

Influence of weather parameters

The multilinear regression of concentration of BaP (ngm^{-3}, in Karlova monitoring station) in respect to meteorological parameters gave statistically significant dependence on temperature T (°C) and wind speed U (ms^{-1}) with determination coefficient R^2=0.31 (1)

$$[\mathrm{BaP}] = 3.1 - 0.30T - 0.13U \tag{1}$$

Thus, the concentrations are negatively correlated both with temperature and wind speed. Of course, in lower ambient temperatures more heating is needed, which results in higher residential emissions. However, stronger wind increases the need of heating in poorly thermally isolated houses, but on the other hand, stronger wind disperses the ingredients in the air more effectively, which effect obviously prevails. Looking closer at temperature dependence of BaP concentration (Figure 1), we see that temperature determines most of the regression (1). Moreover, it appears that dependence is stronger than linear – determination coefficient improves a lot, if exponential fit is applied instead.

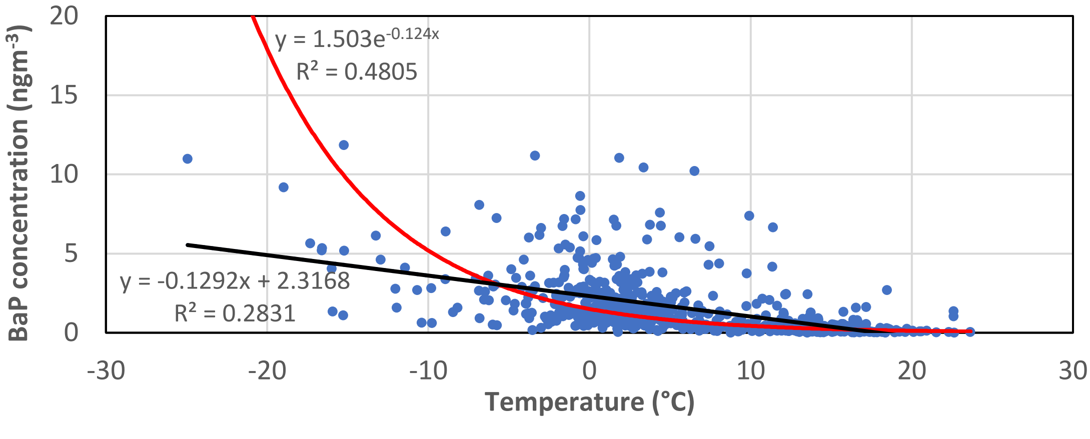

Figure 1. Daily average concentrations of benzo(a)pyrene versus air temperature. Fitted linear trendline is shown in black and exponential trendline in red.

Other air ingredients as proxies to BaP

Another multilinear regression of concentration of BaP (ngm^{-3}) in Karlova monitoring station gives statistically significant dependence on concentrations of CO (ppm) and NO (ppb) with determination coefficient R^2=0.46 (2).

$$[\mathrm{BaP}] = -1.76 + 14.0[\mathrm{CO}] - 0.043[\mathrm{NO}] \tag{2}$$

However, NO_2, SO_2, and even $PM_{2.5}$ do not give statistically important contribution. The regression (2) is almost entirely determined by CO, R^2=0.45 in BaP regression based on CO only. Independent contribution of NO is marginal, but negative, i.e. with higher concentration of NO the concentration of BaP tends to be slightly lower than predicted on the basis of CO only. It was found the wind direction dependences of these pollutants are different: concentrations of BaP and CO are higher with southern and western winds (from direction of massive residential heating), but NO is highest, *vice versa*, with eastern wind – from direction, where a major street traffic crossing is situated. Thus, impact of different pollution sources is expected behind opposite contribution of CO and NO.

Model results and validation

Comparison of measured and modelled concentrations of BaP for the permanent and both temporary monitoring stations is given in Table 1. Annual course of modelled and measured concentrations in Karlova in 2017 (292 daily averages, i.e. 80% of days) is shown in Figure 2.

Table 1. Summary statistics of measured and modelled concentrations of benzo(a)pyrene (ngm^{-3}).

Station	N	Average		Standard dev.		Regression R^2
		measured	modelled	measured	modelled	
South Karlova (permanent)	652	1.64	1.40	2.00	1.42	0.41
North Karlova (temporary)	174	1.57	1.40	1.88	1.31	0.37
Tamme (temporary)	214	1.11	1.78	1.45	1.09	0.38

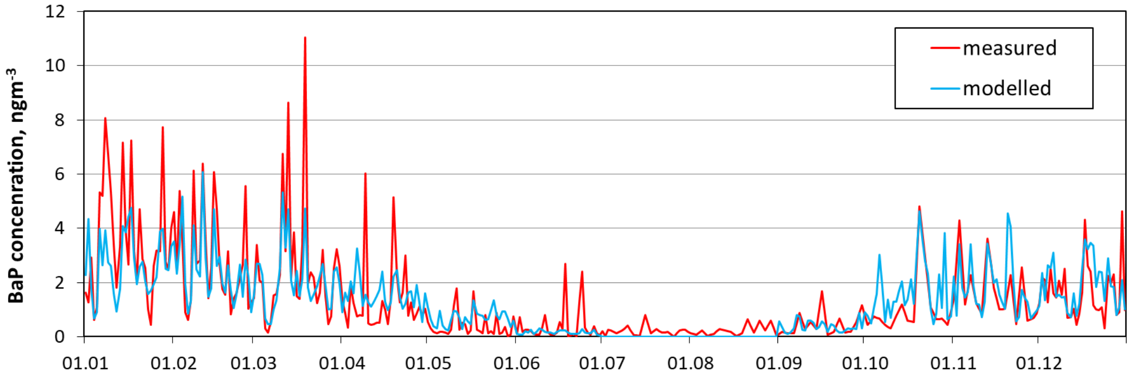

Figure 2. Comparison of measured and modelled annual course of BaP concentration in 2017 (correlation 0.79).

DISCUSSION AND CONCLUSIONS

Assessing the performance of AEROPOL model, it is evident that according to determination coefficient R^2, the model predicts concentrations in South Karlova permanent monitoring station considerably better than the bi-linear regression, based on ambient air temperature and wind speed (Eq. 1). However, the exponential regression (Figure 1) gives even better results, if to exclude the unrealistic high concentrations predicted for temperatures below -17 ºC. On the other hand, the model based on atmospheric physics can predict the gridded concentrations for territory, which was the applied reason of dispersion calculation in this study.

It was found that in South Karlova monitoring station, another product of incomplete burning, carbon monoxide, is a considerable proxy for BaP (Eq. 2). However, the correlation is much lower than with black carbon (BC) (Teinemaa, 2018), but the advantage of CO is that it is monitored permanently on hourly basis and is part of routine ambient monitoring, whereas BC measurements are mostly conducted during special measurement campaigns. The correlation of BaP and CO (and possible impact of NO) in other urban and rural sites is worth of further studies.

In line with European emission inventory (Guerreiro et al., 2015) it was found that residential heating is mostly responsible on high BaP concentrations, whereas contribution of other sources is less than 10% of total emissions and share of these remote emissions in highest concentrations in residential areas is even lower. Thus, the main mitigation strategy is to reduce the residential emissions, making people more aware on both energetic and low-emission advantages of dry wood, reducing the energy consumption of households with more efficient thermal insulation of houses and possibly, transition to central heating in some areas. Installing the automatic air flow control systems and electrostatic precipitators to the furnaces is discussed as well. The governmental and municipal financial support measures for these improvements are suggested.

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