



Short communication

Influence of ozone and meteorological parameters on levels of polycyclic aromatic hydrocarbons in the air



Gordana Pehnc, Ivana Jakovljević*, Anica Šišović, Ivan Bešlić, Vladimira Vadić

Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb, Croatia

ARTICLE INFO

Article history:

Received 12 November 2015

Received in revised form

27 January 2016

Accepted 7 February 2016

Available online 11 February 2016

Keywords:

Meteorology

Multiple linear regression

Ozone

PM₁₀

Seasonal variations

ABSTRACT

Concentrations of ten polycyclic aromatic hydrocarbons (PAHs) in the PM₁₀ particle fraction were measured together with ozone and meteorological parameters at an urban site (Zagreb, Croatia) over a one-year period. Data were subjected to regression analysis in order to determine the relationship between the measured pollutants and selected meteorological variables. All of the PAHs showed seasonal variations with high concentrations in winter and autumn and very low concentrations during summer and spring. All of the ten PAHs concentrations also correlated well with each other. A statistically significant negative correlation was found between the concentrations of PAHs and ozone concentrations and concentrations of PAHs and temperature, as well as a positive correlation between concentrations of PAHs and PM₁₀ mass concentration and relative humidity. Multiple regression analysis showed that concentrations of PM₁₀ and ozone, temperature, relative humidity and pressure accounted for 43–70% of PAHs variability. Concentrations of PM₁₀ and temperature were significant variables for all of the measured PAH's concentrations in all seasons. Ozone concentrations were significant for only some of the PAHs, particularly 6-ring PAHs.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during the incomplete combustion or pyrolysis of organic matter. As some PAHs are proven carcinogens and mutagens, it is necessary to continuously monitor their concentrations in the environment (WHO, 2000). Their potency increases with the number of condensed aromatic rings and maximum genotoxicity is present in PAHs with 5 rings. The potency of PAHs with a higher number of rings is lower, which is explained by their decreased intercellular mobility (IARC, 1984). In the atmosphere, PAHs with a larger number of aromatic rings are mostly bound to particles (Possanzini et al., 2004). Benzo(a)pyrene (5-ring compound) is the most commonly measured PAH and is used as an indicator of carcinogenic hazard in polluted environments. In EU air protection legislation (Directive 2004/107/EC), only benzo(a)pyrene in PM₁₀ particle fraction was given a target value – 1 ng/m³ for an average period of one year. In order to assess the contribution of benzo(a)pyrene in ambient air, measurements of some other relevant PAHs

are also mandatory. The US Environmental Protection Agency (EPA) published a list of 17 priority PAHs in 1995. This list was expanded in 2008 to 28 priority compounds that present a serious hazard for human health (Ravindra et al., 2008).

PAHs usually show significant seasonal variations (Callén et al., 2010; Masiol et al., 2013; Wiriya et al., 2013). Concentrations are higher in winter due to higher emissions during heating season. In summer, concentrations of PAHs in particle fractions are lower because high temperatures enhance the evaporation of PAHs from particle to gas phase, and certain PAHs engage in oxidation and photooxidation reactions with a number of atmospheric chemicals, including ozone (O₃) and nitrogen oxides. Products formed in these reactions are sometimes more dangerous than their parent compounds (IARC, 1983; Kim et al., 2013; National Research Council, 1972; Nikolaou et al., 1984; Takamura-Enya et al., 2006). The most important are nitro-derivatives of PAHs, which can be emitted from a combustion process (e.g., from diesel engines), or formed by photochemical atmospheric reactions of PAHs with NO_x and HNO₃. Oxy-PAHs (ketones, quinones) can be formed by reactions of PAHs with singlet molecular oxygen (National Research Council, 1972) while nitro-oxy-PAHs (nitroketones, nitroquinones) are formed by reactions of PAHs with NO_x and ozone (Schauer et al., 2004).

In previous years, ambient air measurements were mostly

* Corresponding author.

E-mail address: ijakovljevic@imi.hr (I. Jakovljević).

focused on benzo(a)pyrene or on the 16 other US EPA priority PAHs in the PM₁₀ or PM_{2.5} particle fraction (e.g. Slezakova et al., 2013; Teixeira et al., 2013; Varea et al., 2011), with only a few novel studies related to the levels of PAH decomposition products in ambient air (Andreou and Rapsomanikis, 2009; Barrado et al., 2013; Carreras et al., 2013; Souza et al., 2014). Due to the complexity of aerosol chemistry, interactions between PAHs and other air pollutants are still the subject of numerous investigations.

In recent years, the multiple regression method has become a frequent statistical tool for investigating atmospheric processes. When the relationship between variables is linear, multiple linear regression analysis (MLR) can be applied and the regression presented as an equation: $Y = a + b_1X_1 + b_2X_2 + b_3X_3 \dots$; where Y is a dependent (response) variable, X_i are independent variables (predictors), b_i are regression coefficients, and a is an intercept. MLR can be used to gain a better understanding of functional relationships between the dependent and independent variables and to see what might be causing the variation in the dependent variable. It can also be used for the prediction or estimation of unknown variables corresponding to a set of known values (McDonald, 2009).

In the previous decade, MLR was used in studies as a tool for predicting air pollutant levels. For example, Lengyel et al. (2004) used MLR for the prediction of ozone levels using NO₂ and meteorological parameters as input variables. There are only a few papers that used MLR for predicting PAHs concentrations. Callén et al. (2010) used MLR for predicting B(a)P concentrations taking PM₁₀ and selected meteorological variables as possible predictors. Akyüz and Çabuk (2009), for instance, used MLR to predict concentrations of total PAHs bonded to PM_{2.5} and PM₁₀ with respect to PM₁₀ concentrations and meteorological parameters. However, studies performed so far did not include ozone concentrations, or estimate the influence of ozone, even though it is well-known that it has an important role in decomposition of PAHs.

In this study concentrations of ten PAHs in the PM₁₀ particle fraction were measured at an urban site together with PM₁₀ and ozone concentrations. The relationship between the measured pollutants and selected meteorological parameters was analysed using factor analysis and regression analysis. The study was carried out in order to find which variables have the greatest influence on PAH's levels.

2. Materials and methods

2.1. Sampling and PM₁₀ mass measurements

The measuring site (45°50' N, 15°58' E) was in the northern, residential part of Zagreb, Croatia (~800.000 inhabitants), about 20 m from a street with modest traffic density and surrounded by family houses. The heating in the area is mostly on gas or crude oil. Measurements were carried out continuously in the period 1 January–31 December 2009.

The PM₁₀ particle fraction was collected by 24-h sampling on quartz filters with a low volume PM₁₀ Sven Leckel sampler from about 50 m³ of air. Sampling was performed according to European standard EN 12341. The samples were kept frozen in aluminium foil at -18 °C until analysis.

Mass concentrations of PM₁₀ particle fraction were determined gravimetrically according to European standard EN 14907. Before and after the sampling, filters were conditioned at a constant temperature (20 ± 1 °C) and relative air humidity (50 ± 5% RH) for 48 h, prior to the first weighing and reweighing after the next 24 h. Microbalance Mettler TOLEDO MX5 with the resolution of 1 µg was used.

2.2. Sample preparation and analysis of PAHs

Filters were extracted with a solvent mixture of toluene and cyclohexane (7:3) in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness in a mild stream of nitrogen at 30 °C. They were then redissolved in acetonitrile. The analysis was performed using a Varian Pro Star high performance liquid chromatograph (HPLC) with a fluorescence detector and programmed changes in excitation and emission wavelengths (Šišović and Fugaš, 1991; Šišović et al., 2005). PAHs were separated on a Varian stainless steel Pursuit 3 PAH column (100 × 4.6 mm). The mobile phase was a mixture of acetonitrile and water (60:40), and the flow rate was 0.5 mL/min. To prepare calibration curves, a commercial PAHs standard was used (Supelco EPA 610 PAHs Mix). Standard working solutions were obtained by diluting certified solutions with Merck HPLC-grade acetonitrile. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (B(a)A), Chrysene (Chry), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (D(ah)A), benzo(ghi)perylene (B(ghi)P), and indeno(1,2,3-cd) pyrene (IP).

The limit of detection (LD) was determined from the lowest calibration standard and signal/noise ratio according to the equation $LD = 3 \times (C \times N)/S$, where C is the concentration of the lowest calibration standard in ng/µL, N is the noise level in µV, and S is peak height in µV. The detection limit varied from 0.044 ng/mL for Chry to 0.003 ng/µL for Flu. The quantification limit for PAHs in 1000 µL of acetonitrile and 50 m³ of air varied from 0.003 ng/m³ for Chry to 0.2 ng/m³ for Flu. The efficiency of the method was tested using appropriate standard reference material (SRM 1649a, urban dust) provided by the National Institute of Standards and Technology (NIST). Recovery was determined from eight parallel SRM samples and ranged between 70% (B(b)F) and 101% (B(ghi)P).

2.3. Ozone measurements and meteorological data

Ozone concentrations were measured continuously using a HORIBA APOA-360 instrument based on UV photometry, an EU reference method (EN 14625:2005 – “Ambient air quality. Standard method for the measurement of the concentration of ozone by ultraviolet photometry”). From the measured values, 24-h averages were calculated and subjected to further analysis. Meteorological parameters temperature (TEMP), relative humidity (RH), atmospheric pressure (PRESS), wind speed, wind direction and amount of rainfall were obtained from the National Meteorological and Hydrological Service in the form of daily averages.

2.4. Statistical analysis

The STATISTICA 12 software package (StatSoft Inc.) was used for statistical analysis. Calculations were carried out for the whole-year period and for each season separately. Seasonal variations were tested using analysis of variance (ANOVA) and Tukey *post hoc* test. Regression analysis included determination of Pearson's correlation coefficients and multiple linear regression analysis. In MLR analysis individual PAHs (Flu, Pyr, B(a)A, Chry, B(b)F, B(k)F, B(a)P, D(ah)A, B(ghi)P, IP) concentrations were taken as a dependent variable, while independent variables comprised PM₁₀ mass concentration, ozone concentration, temperature, relative humidity and pressure.

Data were also subjected to factor analysis in order to define virtual variables that would describe their interdependence. The factors were based on principal component extraction and rotated by normalized varimax method.

Download English Version:

<https://daneshyari.com/en/article/6336515>

Download Persian Version:

<https://daneshyari.com/article/6336515>

[Daneshyari.com](https://daneshyari.com)