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Identifying risk sources of air contamination by polycyclic aromatic hydrocarbons

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HIGHLIGHTS

- PAH concentrations were measured in air and exhaust gases.
- Marker BghiPe/BaP was used to identify air pollution sources in relation to time.
- Various statistical methods were used precisely to evaluate the BghiPe/BaP ratio.
- In warmer periods, transport is exclusively the source of PAH air pollution.
- In colder periods, local heating stoves contribute to the presence of PAHs in air.

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ABSTRACT

This article is directed to determining concentrations of polycyclic aromatic hydrocarbons (PAHs), which are sorbed to solid particles in the air. Pollution sources were identified on the basis of the ratio of benzo[ghi]perylene (BghiPe) to benzo[*a*]pyrene (BaP). Because various important information is lost by determining the simple ratio of concentrations, least squares linear regression (classic ordinary least squares regression), reduced major axis, orthogonal regression, and Kendall–Theil robust diagnostics were utilized for identification. Statistical evaluation using all aforementioned methods demonstrated different ratios of the monitored PAHs in the intervals examined during warmer and colder periods. Analogous outputs were provided by comparing gradients of the emission factors acquired from the measured concentrations of BghiPe and BaP in motor vehicle exhaust gases. Based on these outputs, it was possible plausibly to state that the influence of burning organic fuels in heating stoves is prevalent in colder periods whereas in warmer periods transport was the exclusive source because other sources of PAH emissions were not found in the examined locations.

1. Introduction

Effectively executed protection of a population consists in the first phase of identifying the sources of hazards followed by qualitative and semi-quantitative estimation or quantitative calculation of those risks resulting from the identified sources of hazards, delimiting critical risks, and finally proposing measures for their mitigation (Božek and Urban, 2008). Serious sources of hazards currently include air pollution, to which contamination by natural sources (forest fires, volcanic eruptions) contribute in part but which in recent decades is mainly due to anthropogenic sources (Villar-Vidal et al., 2014). Important anthropogenic sources of pollution include in particular industry, energy, transport, agricultural production, communal waste incinerators, oil spills, but also to a considerable degree domestic heating stoves. There are,

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therefore, a number of pollutants in the air which present a considerable health risk to human populations and a threat to ecosystems, especially in the vicinity of busy roads and cities with high concentrations of people and industry (Bozek et al., 2011; Liu et al., 2015).

A priority condition for successfully minimizing risks from contaminated air in heavily polluted locations is thus identification of the relevant sources of such pollution. This can be carried out in various ways.

2. Analysis of the current state

Basic approaches to deciding about origins of emission sources essentially comprise the following:

a) morphological and dimensional determination of a complex mixture of captured solid particles (Goldstein et al., 1992; Leal et al., 2014),
b) examination of the physical properties and chemical composition of solid particles (Leal et al., 2014; Winifred et al., 2016),
c) receptor modelling (Dutton et al., 2010),
d) measurement of characteristic markers consisting in the chemical composition of selected contaminants bound to dust particles.

Use of the ratios of various polycyclic aromatic hydrocarbons (PAHs) is the most commonly encountered method in identifying emission sources on the basis of aerosol chemical composition. That is because PAHs are omnipresent, form a broad group of compounds, and many of them demonstrate toxic, mutagenic, teratogenic, carcinogenic, and embryotoxic properties (Haritash and Kaushik, 2009). For the given purpose, benzo[*a*]pyrene (BaP) seems to be an especially suitable PAH due to its being stable while also demonstrating a relatively consistent and high contribution to PAHs' carcinogenic activity (Hailwood et al., 2001). The ratios of its concentration to benzo[ghi]perylene (BghiPe) (Gustafsson and Gschwend, 1997) and to benzo[e]pyrene (Yang et al., 2006) are frequently used as markers for identifying sources of pollution. The ratios of indeno[1,2,3-*cd*]pyrene (IPy) to the sum of concentrations of IPy and BghiPe (Yang et al., 2006), fluoranthene to pyrene, and phenanthrene to anthracene (Kocourek et al., 2003) are also applied. Broad overviews of organic markers, including PAHs, which may be used for identifying sources of atmospheric aerosols were completed by Genualdi (2008) and Křůmal et al. (2012).

Mere monitoring of pollutant concentrations ratios in the atmosphere can, however, lead to losing a good deal of valuable information in relation to specifying pollution sources. For example, Chuesaard et al. (2014) demonstrated through a more detailed examination fluctuations in the BghiPe/BaP ratio within the interval 1.07 to 3.29 as a function of air humidity. They explained decrease in the BghiPe/BaP ratio in dry periods by a contribution of emissions from biomass combustion. As an indicator for assessing the contribution of biomass combustion they proposed the ratio of 9-nitroanthracene and 1-nitropyrene. In parallel, dependencies of organic markers on variables other than air humidity can be found in the literature as can discrepancies in presenting their values for a given pollution source (Genualdi, 2008).

The application of statistical methods in processing measured data is one possibility for resolving existing ambiguities, expanding knowledge in this area, and increasing the precision of markers of specific sources of air contamination under various conditions. In the present article, some statistical procedures which can be applied effectively also for more exact characterization of other markers of this type are presented for evaluating relationships between BaP and BghiPe concentrations in the vicinity of busy urban roads.

3. Methods and devices applied

BaP and BghiPe concentrations were measured in the air of two urban locations. BaP and BghiPe emission factors were determined in exhaust gases of four passenger motor vehicles. The acquired results became the basis for identifying air pollution sources using selected statistical methods.

3.1. Statistical methods

Pollution sources were identified by comparing the regression lines of BghiPe versus BaP. According to our previous findings, using only the ratio of their concentrations leads to a loss of certain important information. We used the linear regression module of the statistical program package QC. Expert to evaluate the results of classic ordinary least squares (OLS) regressions (Kupka, 2013). The fact that BaP concentrations display a smaller error of determination than do BghiPe concentrations was an argument for selecting the model in the form of Equation (1), where c_{BghiPe} and c_{BaP} represent the concentrations of BghiPe and BaP, respectively, and b_1 and b_0 represent the coefficients of the linear term and absolute term, respectively.

$$c_{BghiPe} = b_0 + b_1 \times c_{BaP} \quad (1)$$

The model's reliability and regression parameter estimates were verified using the multiple correlation coefficient *R*, coefficient of determination R^2, predicted correlation coefficient R_p, mean squared prediction error *MSPE*, and the Akaike information criterion. The legitimacy of using the linear model was tested using the Fisher–Snedecor significance test, Scott multicollinearity criterion, Cook–Weisberg heteroscedasticity test, Jarque–Bera normality test, Wald and Durbin–Watson autocorrelation tests, and the residual sign test (Meloun and Militký, 2004).

The robust method by Kendall and Theil, which is not sensitive to outlying values, was subsequently applied. The Kendall–Theil Robust Line software is a Visual Basic program that may be used with the Microsoft Windows operating system to calculate parameters for robust, nonparametric estimates of linear regression coefficients between two continuous variables (Granato, 2006). The slope of the line was calculated as the median of all possible pairwise slopes between points. The intercept was calculated so that the line runs through the median of input data. The confidence interval of the slope was calculated, as well.

Because it could not be expected for the OLS regression to display an error close to zero, the reduced major axis (RMA) method was used to verify the results' reliability (Turner et al., 2009; Friedman et al., 2013) using RMA software (Bohonak, 2004). The method consists in concurrent minimization of both the *y* and *x* axes residuals. The classical linear model (RMA L) and a model based on the jackknife method (RMA JK) were applied in the study. In parallel, the orthogonal regression (OR) method was included in the program Number Cruncher Statistical System (NCSS) based on minimization of the perpendicular distance of regression points from the regression line (Hintze, 2007).

3.2. Measurement of emissions

Air samples were collected over a period of 24 h using a medium-volume Leckel MVS6 sampler and, similarly, the procedure presented in our previous publication (Bozek et al., 2016) was