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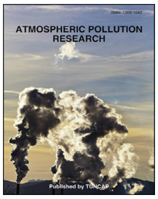

Original article

Source apportionment with uncertainty estimates of fine particulate matter in Ostrava, Czech Republic using Positive Matrix Factorization

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ABSTRACT

A 14-week investigation during a warm and cold seasons was conducted to improve understanding of air pollution sources that might be impacting air quality in Ostrava, the Czech Republic. Fine particulate matter ($PM_{2.5}$) samples were collected in consecutive 12-h day and night increments during spring and fall 2012 sampling campaigns. Sampling sites were strategically located to evaluate conditions in close proximity of a large steel works industrial complex, as well as away from direct influence of the industrial complex. These samples were analyzed for metals and other elements, organic and elemental (black) carbon, and polycyclic aromatic hydrocarbons (PAHs). The $PM_{2.5}$ samples were supplemented with pollutant gases and meteorological parameters. We applied the EPA PMF v5.1 model with uncertainty estimate features to the Ostrava data set. Using the model's bootstrapping procedure and other considerations, six factors were determined to provide the optimum solution. Each model run consisted of 100 iterations to ensure that the solution represents a global minimum. The resulting factors were identified as representing coal (power plants), mixed Cl, crustal, industrial 1 (alkali metals and PAHs), industrial 2 (transition metals), and home heat/transportation. The home heating source is thought to be largely domestic boilers burning low quality fuels such as lignite, wood, and domestic waste. Transportation-related combustion emissions could not be resolved as a separate factor. Uncertainty estimates support the general conclusion that the factors identified as representing coal power and home heat/transportation dominate the percent contribution to fine mass. Apportionment of regulated individual species is also presented.

1. Introduction

Despite efforts to improve air quality, mostly through emissions reductions from the power generation and industrial sectors, the Ostrava region of the Czech Republic continues to experience episodes of high pollutant concentrations, especially during the fall and winter seasons. This region of the Czech Republic is located in a valley southwest of the Silesian region of Poland, which has among the highest levels of air pollution in Europe (EEA, 2014). A study in the Silesian region of Poland attributed much of the fine particle concentrations to emissions from domestic furnaces (burning coal, biomass, and household waste) and auto emissions (Rogula-Koslowska et al., 2013).

Ostrava is home to the largest steel works facility in the Czech Republic. Concentrations of particulate matter and benzo(a)pyrene (BaP) measured at a permanent measuring station (Radvanice) downwind from the industrial complex (based on prevailing winds) are higher than at other locations in Ostrava. The BaP is of particular concern due to its carcinogenic potential (ATSDR, 1995). In a recent investigation of the impact of air pollution on human health in the Ostrava-Radvanice region, Sram et al., 2013 provided evidence of an association between industrial pollution and deteriorated health and identified BaP as posing a significant health risk.

In addition to steel production and other industries, major sources of air pollutants in the region encompassing Ostrava as well

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Abbreviations: FL, fluorene; PHE, phenanthrene; ANT, anthracene; FLA, fluoranthene; PYR, pyrene; BaA, benzo(a)anthracene; CHR, chrysene; BbF, benzo(b)fluoranthene; BkF, benzo(k)fluoranthene; BaP, benzo(a)pyrene; I123cdP, indeno(1,2,3c,d)pyrene; DBahA, dibenzo(a,h)anthracene; BghiPRL, benzo(g,h,i)perylene; BC, black carbon; EC, elemental carbon; OC, organic carbon.

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as upper Silesia in Poland include coal-fired power plants, which provide power-generation for domestic and industrial use; home heating by a variety of fuel types including natural gas, coal, wood, and domestic waste; and transportation, primarily cars and buses fueled by standard gasoline and diesel fuel (Ministry of the Environment of the Czech Republic, 2013; EEA, 2014).

The Czech Hydrometeorological Institute (CHMI) in collaboration with the U.S. Environmental Protection Agency (EPA) conducted a short-term multi-season investigation to improve understanding of air pollution sources impacting the Ostrava air quality. A study description and qualitative overview of the data have been presented elsewhere (Vossler et al., 2015). This paper reports on quantitative contributions of sources to measured pollutants obtained from Positive Matrix Factorization (PMF) source apportionment modeling of the data, and demonstrates the uncertainty estimate methods included in the model (Paatero et al., 2014). The new version of EPA's PMF software v5.1 (Norris et al., 2015) includes a classical bootstrap method to capture random error, and a method that computes a range of possible solutions based on the displacement of factor species values. The two methods can also be combined to capture the uncertainty due to random errors and rotational ambiguity.

2. Methods

The principal focus of the study is on the composition of the fine particulate matter used in source apportionment modeling to evaluate relative source impacts on the air quality in Ostrava. Details of the sample collection and analysis, including all relevant references, are provided in Vossler et al., 2015. A summary of methods is presented here.

2.1. Sampling, measurements, and monitoring

Fine particulate matter ($PM_{2.5}$) samples were collected in consecutive 12-h daytime and night-time increments during “spring” (5/14/2012 through 7/1/2012) and “fall” (10/17/2012 through 12/6/2012) to capture emissions from two distinct seasons. Sampling sites were strategically located to evaluate conditions in close proximity of a large steel works industrial complex, as well as away from direct influence of the industrial complex (Fig. S1 in the supporting material). Radvanice is a suburban industrial site downwind of prevailing winds from the industrial complex; Vratimov is a residential site upwind of prevailing winds from the industrial complex; Poruba is representative of the Ostrava area while being more removed from direct influence of the steel manufacturing industrial complex or other major point sources.

Analyses of particulate samples included gravimetric mass, x-ray fluorescence elemental analyses, black carbon (BC) via transmissometer measurements, and organic carbon (OC) and elemental carbon (EC) concentrations via a thermal-optical method. The combined particulate and gas phase concentrations for 14 polycyclic aromatic hydrocarbon (PAH) compounds were determined via gas chromatography-mass spectrometry (GC–MS).

The particulate matter samples were supplemented with continuous SO_2 monitoring at all three sites, and PM_{10} and additional pollutant gas monitoring (O_3, NO, NO_2, NO_X, CO, benzene) at the Radvanice and Vratimov sites. Meteorological measurements including wind speed and direction were operated at the Vratimov and Radvanice sites, as well as at the permanent meteorological stations located throughout the region.

2.2. Positive Matrix Factorization (PMF) receptor modeling

Source apportionment models are mathematical methods for quantifying the contribution of sources to the pollutant concentrations at one or more sampling sites. Positive Matrix Factorization (PMF) is one of a class of source apportionment models that computes the best combination of non-negative factor contributions and factor profiles that reproduces the input data matrix (containing the measured pollutant concentrations) while minimizing the residual, represented by Q in the central PMF equation (presented in Text S1 in the supporting material along with other model fundamentals). PMF requires that no sample can have a significantly negative source contribution, and individual data points are weighted according to their reported uncertainties (Paatero et al., 2014). The PMF model is described in detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997; Paatero et al., 2005). We applied the EPA PMF model (Norris et al., 2015) version 5.1 to the Ostrava data set.

2.3. Determining the optimum base run scenario

Samples may be excluded from the base run based on missing values, extreme values, or other reasons as determined to meet modeling objectives. We chose to exclude from the analysis any sample with at least one missing value, which occurred when one of the filter samples was missing and thus not available for analysis. Thus, 4 Poruba site samples and 6 Vratimov site samples were excluded due to missing values. In addition, 7 samples were selected for exclusion based on previously identified extreme values for at least one measured species (Vossler et al., 2015). Following these sample exclusion choices, less than 3% of sample records were excluded from the modeling computations. A total of 579 samples covering the full data set were retained for the model runs.

PMF v5.1 allows the user to exclude species by categorizing them as “bad”, or down-weight a retained species to “weak”, which triples the provided uncertainty. The model-computed signal-to-noise (S/N) as well as knowledge of analytical and sampling issues are used to guide species weighting. Only concentration values that exceed the uncertainty are included in the calculation of S/N and signal is computed as the difference between concentration and uncertainty. Concentrations with values below uncertainty values are assigned an S/N of zero. PMF guidance suggests that a species be weighted as “weak” if the S/N is greater than 0.5 but less than 1.0, while species with S/N 1.0 or greater should be weighted as “strong”, meaning that the uncertainty values are used in the model without further alteration.

For the Ostrava data set, we excluded all species with S/N of 0.5 or lower. Additional species were excluded despite otherwise acceptable S/N values based on details known about the measurements and other considerations. Sc was excluded because it is a known background element in the EPA XRF system. Mg and Al both have several large negative values that are likely due to the large and variable background for Al in the EPA XRF system and were excluded. Because uncertainties are computed for each XRF element individually, it was assumed that the XRF uncertainties would weight each element appropriately in the model runs and that no down-weighting is needed. Thus, all XRF-measured elements included based on the above criteria were initially weighted as “strong”. To evaluate species weight assignment for the XRF elements, we reviewed the statistics reported for the predicted vs observed scatter plots following an initial model run (Table S1 in the supporting material). Species with an R^2 between 0.1 and 0.5 were considered not reproduced well by the model and re-weighted as “weak”. Thus, As, Se, and Bi were re-classified as