PAHs modelling over urban area of Rome: integration of models results with experimental data

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Abstract

The identification and quantification of population exposure of children and elderly people to PAHs in urban areas are the major goals of the EXPAH LIFE+ Project (www.ispesl.it/expah). To reach these objectives an integrated approach, based on measurements and modeling techniques, has been set up to preliminarily reconstruct PAHs levels in the Rome metropolitan area. Field campaigns of particulate PAHs and $PM_{2.5}$ have been performed in different sites and microenvironments from December 2011 to July 2012. These data were essential to evaluate and integrate results of the Flexible Air quality Regional Model (FARM) that has been run from June 2011 to May 2012. PAHs modeled concentrations are presented for the city of Rome as well as a comparison with observations. Capabilities and limits in modeling PAHs in urban areas are then discussed.

1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of complex organic chemicals of increasing concern for their occurrence in the environment, produced by the incomplete combustion of organic material. PAHs can be found in the atmosphere in both gaseous and particulate forms. The best known PAH is the benzo[a]pyrene (B[a]P). DNA damage induced by PAHs exposure was demonstrated by different authors (eg. Taioli et al., 2007). PAHs are emitted by many sources, including motor vehicles, domestic burning of coal and wood, power generation via combustion and waste processing. In highly urbanized areas the sources are almost exclusively anthropogenic: domestic heating and mobile (vehicles) sources (Ravindra et al, 2008). Population living in urban areas, where elevated levels are typically found (in the range of ng m^{-3}), have a significant risk to contract lung, skin, and bladder cancers due to the exposure to these pollutants. The identification and quantification of population exposure of children and elderly people to PAHs in urban areas are the major goals of the EXPAH LIFE+ Project (www.ispesl.it/expah). To reach these objectives an integrated approach, based on measurements and modeling techniques, has been set up to preliminarily reconstruct PAHs levels in the Rome metropolitan area. In this paper PAHs modeled concentrations are presented for the city of Rome as well as a comparison with observations.

2 Material and methods

2.1 Inclusion of PAHs processes in FARM model

The Atmospheric Modelling System (AMS) used to reconstruct PAHs levels is based on FARM (Flexible Air quality Regional Model; Gariazzo *et al.*, 2007), a three-dimensional Eulerian chemical-transport model that accounts for the transport, chemical conversion and deposition of atmospheric pollutants. Among PAHs, four indicator compounds, considered by the UNECE Protocol on POPs on the basis of their low volatility combined to their carcinogenicity, have been included in the model: namely benzo(a)pyrene (B[a]P), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F) and indeno(1,2,3-cd)pyrene (I_P). The SAPRC-99 gas-phase chemical mechanism and the modal AERO3 aerosol module (U.S. EPA CMAQ modeling system), have been consequently updated in order to include the PAHs reactions with hydroxyl radical (Gusev *et al.*, 2005) and their partitioning between gas and aerosol phases following the approach suggested by Aulinger *et al.* (2007).

2.2 Study area and PAHs emission inventory

Rome, one of the greatest urbanized cities of the Mediterranean area with an extension of 1,290 km^2 and about 3 million inhabitants, has been selected as a target site for a detailed study of population exposure of children and elderly people to PAHs. The air pollution in the city is mainly characterized by high levels of NO_2, O_3 and PM_{10}. Several studies have reported severe health effects due to air pollution in this urban area (Cesaroni *et al.*, 2013). In order to estimate PAHs levels over this area, FARM has been applied to two nested domains: a larger domain including Lazio Region (61 x 51 grid cells with an horizontal resolution of 4 km) and the target domain including Rome metropolitan area (60 x 60 cells with an horizontal resolution of 1 km). Emission data have been derived from the Lazio Region inventory and from the reference national emission inventory ISPRA2005. The latter has been used to assign emission data to surrounding regions included in the larger domain and has been updated to the year 2009, coherently with the regional inventory, using historical trends. Details about the PAHs emission inventory can be found in a proper EXPAH technical report (Radice *et al.*, 2012). Spatial disaggregation, time modulation and speciation (for PAHs, VOCs and PM) of emission data were made according to thematic layers (eg. EU CORINE Land Cover), typical trends (yearly, monthly and daily) and speciation profiles depending on SNAP source classification. The analysis of PAHs emissions over Lazio Region, Rome Province and Rome Municipality evidences that residential heating represents by far the major source accounting for 73% (which corresponds to 4389 kg/year), 86% (3086 kg/year) and 92% (2010 kg/year), respectively. Waste treatment contribution is the second main contribution with 22% of emissions over the Region (1310 kg/year), 9% over the province (334 kg/year) and 3% over Rome municipality (64 kg/year). Road transport contributes to PAHs emissions in the 3-4% range over these areas. PAHs emissions have been also compared with the European scale inventory developed by TNO evidencing the significant uncertainty affecting these data that can generally be considered larger than that associated to the other pollutants.

2.3 PAHs monitoring field campaigns

Experimental campaigns have been performed in the frame of EXPAH project with the aim to measure PAHs and $PM_{2.5}$ at different living/working microenvironments in Rome. $PM_{2.5}$ was sampled, on a daily basis, at low volume conditions using PTFE filters, and then analysed for higher carcinogenic PAH contents by means of gas chromatography/mass spectrometry, using five days aggregated sampled filters to increase signal-noise ratio. Two seasonal in-field campaigns (summer (May-July 2012) and winter-spring (December 2011 - March 2012)) have been performed by sampling both indoor and outdoor living/working microenvironments. During each seasonal campaign, 20 living environments have been monitored among houses, schools, offices and transport vehicles. In winter-spring in-field campaign, B[a]P outdoor levels ranged from 1.4 and 2.0 ng/m^3, while target PAHs ranged 8.4÷13.2 ng/m^3. At summer lower levels have been measured: the ambient air B[a]P ranged from 0.06 to 0.19 ng/m^3, while PAHs ranged 0.62÷1.52 ng/m^3.

3 Results and discussion

The simulation period lasted from June 2011 to May 2012 including almost all EXPAH experimental campaigns. Meteorological fields needed by FARM have been reconstructed by the limited area non-hydrostatic weather prediction model RAMS driven by ECMWF analyses. Measured data collected during the experimental campaigns permitted to evaluate the performance of the modeling system during different periods of the year. The comparison between observed and predicted PAHs concentrations has evidenced the capability of the modeling system to reconstruct PAHs concentration levels over Rome conurbation and to describe their seasonal variation (see Figure 1). Nonetheless, an overestimation of observed concentrations was identified during colder periods probably determined by: 1) the large uncertainty affecting PAHs emission estimates from the house heating sector due to the significant emission factors variations depending on the fuel burned; 2) difficulties in distributing emissions within the urban texture.

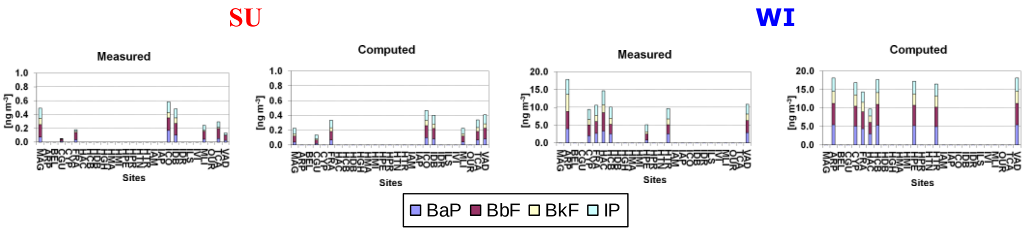

Figure 1. Observed and computed PAHs concentrations during summer (SU: August, 2-7, 2011) and winter (WI: January, 16-20 2012) at monitoring sites (x-axis) operating during EXPAH field campaigns.

To reduce model uncertainty and obtain more reliable gridded pollution fields for further epidemiological studies, two approaches, based on “data fusion” techniques and on a simplified method have been used. The former combines background concentration fields with observed information using Successive Correction Method (SCM) (Bratseth, 1986).The latter consists in multiplying daily PAHs concentrations by a correction factor computed as the ratio between observed and predicted monthly average concentrations (f_c). In Table 1, the statistical analysis for B[a]P is presented, confirming the capability of the adopted approaches to improve model result.

Table 1. Statistical analysis of simulated yearly averaged B[a]P concentrations over Rome. Bold values in parenthesis are referred to ideal values of the considered metrics.

Run	**IOA (1)**	**R (1)**	**FAC2 (100 %)**	**MFE (0 %)**	**RMSE (0 ng m^{-3})**
Base Case	0.59	0.67	44.4	79.3	1.45
Data fusion	0.95	0.83	93.0	25.1	0.20
f_c	0.79	0.67	80.7	39.3	0.35

Nevertheless, since EXPAH measurement field campaigns did not cover the whole modeled year and PAHs are not routinely measured at the stations of the local monitoring network, the data fusion approach could not be used to reduce predicted concentrations bias along the simulated year. So the "f_c" approach has been considered to provide more realistic concentration fields.

4 Conclusions

The upgraded version of FARM model, including PAHs chemistry, has been applied to Rome metropolitan area (1 km resolution) from June 2011 to May 2012 (1 year run). This application represents one of the earlier high resolution simulations performed over one of the mostly significant urban area in Europe. PAHs results evidenced the capability of the modeling system to reconstruct their levels over Rome conurbation and to describe their seasonal variation. However, since an overestimation of observed values has been identified during colder periods, possibly due to inaccuracies in the PAHs emission inventory, a simplified approach, consisting in multiplying predicted concentrations by a monthly correction factor, has been adopted to reduce PAHs concentrations bias. This correction provided an improvement of model results confirmed by the statistical analysis. Results addresses for an improvement of PAHs emission inventory and its speciation.

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