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Benzo[a]pyrene modelling over Italy: comparison with experimental data and source apportionment

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ABSTRACT

This work describes the extension of the Flexible Air quality Regional Model (FARM) to polycyclic aromatic hydrocarbons (PAHs). Modules accounting for the partitioning of these species between gaseous and particulate phases were inserted in a simplified version of the model and in a more state–of–the–art configuration implementing the SAPRC99 gas–phase chemical mechanism coupled with the *aero3* aerosol module. Both versions of FARM were applied over Italy for the year 2005. The analysis of model results was focused on benzo[a]pyrene (B[a]P), which is considered a marker substance for the carcinogenic risk of PAHs. Simulated B[a]P concentrations were compared with observed data, collected at background sites mainly located in Po Valley, and with concentrations produced at continental scale by EMEP/MSC–E model. Higher B[a]P yearly average concentrations were simulated by the national modelling system as a result of different factors: the higher resolution adopted by the national modelling system, the greater Italian emissions estimated by the national inventory and the effects induced by the use of a high resolution topography on meteorological fields and thus on the dispersion of pollutants. The comparison between observed and predicted monthly averaged concentrations evidenced the capability of the two versions of FARM model to capture the seasonal behaviour of B[a]P, characterised by higher values during the winter season due to the large use of wood for residential heating, enhanced by lower dispersion atmospheric conditions. The statistical analysis evidenced, for both versions of the model, a good performance and better indicators than those associated to EMEP/MSC–E simulations. A source apportionment was then carried out using the simplified version of the model, which proved to perform similarly to the full chemistry version but with the advantage to be computationally less expensive. The analysis revealed a significant influence of national sources on B[a]P concentrations, with non–industrial combustion employing wood burning devices being the most important sector. The contribution of the industrial sectors is relevant around major industrial facilities, with the largest absolute contribution in Taranto (above 1 ng m^{-3}), where steel industries are the largest individual source of PAHs in the country.

1. Introduction

The United Nations Economic Commission for Europe (UNECE), set up in 1947 to promote pan–European economic integration, signed in 1979 the Convention on Long–range Transboundary Air Pollution (CLRTAP) with the aim to protect the human environment against air pollution. The Convention entered into force in 1983 and over the past 30 years it has been extended by 8 Protocols, targeting sulphur, nitrogen oxides, volatile organic compounds, ammonia, toxic heavy metals and persistent organic pollutants (POPs). POPs are chemical substances that bioaccumulate through the food web and pose a risk of causing adverse effects to human health and the environment. The Protocol on POPs banned the production and the use of some products (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene), restricted the use of some substances (DDT, hexachlorocyclohexane – HCH – and PCBs) and required the parties to reduce their emissions of dioxins (PCDD), furans (PCDF), hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs). PAHs are a group of chemicals released during the incomplete burning of oil, coal, gas and other organic materials such as trees during forest fires. Significant sources of PAHs include domestic combustion, vehicle exhausts,

production sites of metals, coke and asphalt, and power stations. PAHs consist of fused benzene rings, containing only carbon and hydrogen, that can be found in the atmosphere in gas–phase (2–ring, e.g. naphthalene, highly volatile), in particulate forms (5–ring, e.g. benzo[*a*]pyrene – B[a]P, weakly volatile) and distributed between gas and particle phases (3– and 4–ring, e.g. phenanthrene, pyrene, semivolatile) (Finlayson–Pitts and Pitts, 1999). They are ubiquitous in ambient air and some of them have been identified as suspected carcinogens (IARC, 1983; IARC, 1987). The US Agency for Toxic Substances and Disease Registry (ATSDR, 1995) has considered 17 priority PAHs, on the basis of their toxicological profile, availability of information, suspect of harmful effects, greater population exposure and high ambient concentrations. Since PAHs are actually a group of over 100 different chemicals (Zedeck, 1980), the Protocol on POPs has considered to focus on four indicator compounds, chosen on the basis of their low volatility combined to their carcinogenicity: benzo[*a*]pyrene, benzo[*b*]fluoranthene (B[b]F), benzo[*k*]fluoranthene (B[k]F) and indeno[1,2,3–*cd*]pyrene (I_P). Benzo[*a*]pyrene is the best known PAH and according to the European Directive 2004/107/EC it "*should be used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in ambient air*". This Directive set up a "target value" ("*a concentration in the ambient air fixed with the*

aim of avoiding, preventing or reducing harmful effects on human health and the environment as a whole, to be attained where possible over a given period") of 1 ng m^{-3} for the total content of B[a]P in the PM$_{10}$ fraction averaged over a calendar year. Modelling of selected POPs and heavy metals (HMs) is carried out, under CLRTAP, at the Meteorological Synthesizing Centre East (MSC–E) of the European Monitoring and Evaluation Programme (EMEP), the executive body of the Convention investigating and evaluating long–range transport of air pollution over Europe. An intercomparison study of different model approaches for a better understanding of the POPs behaviour in various environmental compartments (Shatalov et al., 2000), has evidenced the relevance of deposition processes (dry deposition of particles and wet deposition) and gaseous exchange processes between atmosphere and underlying surfaces on predicted air concentrations. Due to the increasing interest on the fate of POPs in different ecosystems, modules dedicated to their treatment have been included in existing air quality models. A new version of the Community Multiscale Air Quality modeling system (CMAQ) implementing a module that accounts for the partitioning of semivolatile organic compounds, particularly PAHs, between the gaseous and the particulate phases, is presented by Aulinger et al. (2007). Sehili and Lammel (2007) performed model experiments with the atmospheric general circulation model ECHAM5, including gas–particle partitioning and degradability by reaction with ozone, hydroxyl and nitrate radicals for two PAHs: benzo[a]pyrene and fluoranthene. Matthias et al. (2009) investigated the levels of B[a]P concentrations in ambient air in Europe, using an expanded version of CMAQ, evidencing an underestimation of observed values (on average by 50%) and its capability to capture the temporal evolution and the regional distribution of this pollutant. More recently Zhang et al. (2011) applied a modified version of the CanMETOP model to simulate the transport and outflow of PAHs emitted from China and evidenced the influence of emissions and meteorological conditions on the spatial distributions of PAH levels in the atmosphere.

To investigate the distribution of B[a]P over the Italian territory and to set up proper emission control strategies, the National Ministry of Environment has sponsored the extension of the "National modelling system for supporting the international negotiation process on air pollution and assessing air quality policies at national/regional level" (MINNI Project; Zanini et al., 2005) to this pollutant. This paper describes the extension to PAHs of the Flexible Air quality Regional Model (FARM, Silibello et al., 2008), the air quality model of MINNI project, and its application over Italy for the year 2005. Section 2 describes two approaches adopted to implement PAHs chemistry in the model, while Section 3 describes the simulation setup; Section 4 focuses on the results of B[a]P simulations and show comparison with the observations and with the results of EMEP/MSC–E model; Section 5 illustrates the analysis of the contributions of foreign sources and sector activities on estimated B[a]P concentrations.

2. Model Description

FARM is a three–dimensional Eulerian chemical–transport model employed in various applications from local to regional scales (Gariazzo et al., 2007; Calori et al., 2008; Kukkonen et al., 2012). Two configurations of the model have been considered in this work (see the Supporting Material-SM for more detail):

(1) a simplified gas–phase mechanism derived from the EMEP Lagrangian Acid Deposition Model (Hov et al., 1988; EMEP, 2003) coupled with a bulk aerosol module;

(2) the SAPRC99 gas–phase chemical mechanism (Carter, 1999) coupled with the *aero3* aerosol module, implemented in CMAQ (Binkowski, 1999).

These gas–phase chemical mechanisms have then been extended in order to include PAHs considered by the Protocol on POPs, i.e. 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 gas–phase reactions of these pollutants with the hydroxyl radical represent a very effective sink (Gusev et al., 2005), and are described by the following second order equation:

$$\frac{d[PAH]}{dt} = -K \cdot [PAH] \cdot [OH] \tag{1}$$

where [PAH] is the concentration of a generic congener in air [molec cm^{-3}], [OH] the concentration of OH radical [molec cm^{-3}] and K the degradation rate constant [cm^3 molec^{-1} s^1], assigned according to Meylan and Howard (1993). Hereafter, we refer to these configurations of FARM model respectively with the terms ACID–PAHs and SAPRC99–PAHs.

2.1. Gas–aerosol partitioning of PAHs

As stated by Finizio et al. (1997), there is some debate whether the POPs partitioning between the gaseous and particulate phase (sorption process) is adsorption or absorption, or both. When particulate is mainly constituted by mineral material, simple physical adsorption will dominate the sorption process, while absorption process seems to be more relevant when particulate matter contains organic matter from primary emissions and from the formation of secondary aerosols (Pankow, 1994). The adsorption process to mineral surfaces is represented using the Junge–Pankow model (Junge, 1977; Pankow, 1987), based on subcooled liquid vapour pressure p_{OL} (Pa), while the absorption process is characterized by the octanol–air partition coefficient K_{OA}, that is a valuable direct descriptor of semi–volatile organic chemicals (Harner et al., 1999). Calling a and g respectively the aerosol–associated and gaseous concentration of a given semi–volatile organic chemical (ng m^{-3}), the fraction of PAH sorbed on tropospheric aerosol particles, φ is given by:

$$\varphi = \frac{a}{a+g} = \begin{cases} \varphi^{ad} = \dfrac{c \cdot \vartheta}{(p_{OL} + c \cdot \vartheta)} \\ \varphi^{ab} = \dfrac{K_P^{OC} \cdot TSP}{1 + K_P^{OC} \cdot TSP} \end{cases} \tag{2}$$

In the adsorption relationship (φ^{ad}), c is a constant dependant on the thermodynamic parameters of the adsorption process and on the properties of aerosol particle surface [a value of 0.17 (Pa m) is assumed for this parameter; Junge, 1977] and ϑ is the specific surface of aerosol particles (m^2 m^{-3}). In the absorption expression (φ^{ab}), TSP represents the concentration of suspended particulate material (μg m^{-3}) and K_p^{oc} the gas–particle partitioning coefficient (m^3 μg^{-1}), defined as:

$$K_p^{OC} \approx \frac{10^{-9} K_{OA} f_{om}}{\rho_{OCT}} \tag{3}$$

where f_{om} is the fraction of the particle mass that consist of absorbing organic matter and ρ_{OCT} is the density of octanol (820 kg m^{-3}).

With the *aero3* aerosol module the absorption of PAHs into aerosol water is also considered by introducing the following partitioning coefficient:

$$K_p^{aq} \approx \frac{10^{-9} K_{wa} f_w}{\rho_{wa}} \tag{4}$$

where f_w is the fraction of the particle mass that consists of water, ρ_{wa} is the density of water and K_{wa} the water–air partitioning coefficient, which is equal to the inverse of dimensionless Henry's law constant. According to Aulinger et al. (2007), the absorption into aerosol water is considered when the aerosol can be treated as wet, a condition that occurs when the ratio of aerosol water to ammonium sulfate exceeds the solubility of ammonium sulfate, considered the major compound in mineral aerosols. In such condition, all inorganic ions are dissolved and no adsorption to inorganic material can take place. The partitioning of PAHs between Aitken (I) and accumulation (J) modes is simulated as follows (Aulinger et al., 2007):

$$a_I = \varphi_I\left(a_I + g\right) = \varphi_I\left(a_I + c_{tot} - a_I - a_J\right) = \varphi_I\left(c_{tot} - a_J\right)$$
$$a_J = \varphi_J\left(a_J + g\right) = \varphi_J\left(a_J + c_{tot} - a_I - a_J\right) = \varphi_J\left(c_{tot} - a_I\right)$$

(5)

where $\varphi_{I,J}$ is the particulate fraction of the compound in the two modes due to the sum of the sorption processes (e.g., $\varphi_{I,J} = \varphi_{I,J}^{ad} + \varphi_{I,J}^{ab,OC} + \varphi_{I,J}^{ab,aq}$) and the gaseous concentration g has been replaced by the mass consistent constraint relationship: $g = c_{tot} - a_I - a_J$. In matrix form the system has the following expression:

$$\begin{bmatrix} 1 & \varphi_I \\ \varphi_J & 1 \end{bmatrix} \cdot \begin{bmatrix} a_I \\ a_J \end{bmatrix} = c_{tot} \cdot \begin{bmatrix} \varphi_I \\ \varphi_J \end{bmatrix}$$

(6)

whose solutions are:

$$a_I = c_{tot} \cdot \varphi_I \cdot \frac{1 - \varphi_J}{1 - \varphi_I \varphi_J}$$
$$a_J = c_{tot} \cdot \varphi_J \cdot \frac{1 - \varphi_I}{1 - \varphi_I \varphi_J}$$

(7)

The gaseous concentration g then can be calculated by the above mass–consistent constraint relationship. Intra– and inter–modal coagulation within and between Aitken and accumulation modes is considered for PAHs similarly to the other species considered in these modes.

With the bulk aerosol module (ACID–PAHs) a value of 0.4 is assumed for the parameter f_{om}, while for the specific surface of aerosol particles (ϑ) a value of 1.1×10^{-3} m^2 m^{-3} is adopted when the aerosol concentration is greater than 20 µg m^{-3} and a value of 1.5×10^{-4} m^2 m^{-3} otherwise. With the SAPRC99–PAHs configuration these parameters are computed by the *aero3* aerosol module.

The fraction of PAHs sorbed on fine particles is computed, with both versions of FARM, considering adsorption and absorption processes.

2.2. Deposition of PAHs

According to Gusev et al. (2005), the dry deposition flux of PAHs in the gas–phase is not considered, while the deposition velocity of these species in the particulate phase is set equal to that considered for the fine aerosol components. Wet deposition of PAHs in gaseous and particulate phase is calculated separately. See the SM for more detail about the precipitation scavenging module implemented in FARM.

3. Simulation Setup

The modelling system includes specific modules to reconstruct meteorological fields and related turbulence parameters, to prepare the emission data starting from available inventories and to set initial and boundary concentrations starting from larger scale

model simulations. The configuration chosen for the application over the Italian domain for the year 2005 is described in the following paragraphs. The calculation grid for the air quality model FARM has a horizontal resolution of 20 km and 16 terrain–following levels, irregularly spaced from the ground to 10 000 m above surface level, with the first four layers placed at 20, 75, 150 and 250 m.

3.1. Meteorological input

The meteorological input fields have been produced with the prognostic, non–hydrostatic meteorological model RAMS (Cotton et al., 2003), run in a 2–way nested grids configuration: an outer grid covering a large part of Central Europe and the Mediterranean Sea, with a horizontal resolution of 60 km, and an inner grid, including the Italian domain for the air quality simulations, with a resolution of 20 km. Initial and boundary conditions and data assimilation fields have been based on mesoscale analyses produced by means of the RAMS pre–processor ISAN (ISentropic ANalysis), with a time frequency of 1 hour. ISAN implements an optimal interpolation method based on Barnes algorithm (Barnes, 1964). ECMWF analyses, available every 6 hours with a horizontal resolution of 0.5°, have been used as background fields. WMO (World Meteorological Organisation) SYNOP and METAR surface observations, retrieved from ECMWF archives and available with time frequency of 1 hour, have been used as assimilated data. A nudging technique has been employed by RAMS to assimilate data analyses during the whole model simulation, through an additional forcing term to the conservation equations for pressure, temperature, water vapour and momentum. The sea surface temperature has been defined on a daily basis from data included in ECMWF operational analyses. At the start of every simulation week, RAMS has been re–initialized on the basis of ECMWF analyses and surface observations, to avoid shortcomings due to possible errors in input data, growing with simulation time. RAMS implements also a land ecosystem–atmosphere feedback sub–model for the evaluation of energy and water budgets and fluxes at the earth's surface and their interactions with the atmosphere, so multiple layers prognostic equations for soil temperature and moisture are also included. To limit initialization influence, the initial soil status, on January 1st at 00 UTC, has been obtained from a preliminary model simulation extended to the whole month of December of the previous year. The subsequent simulations have been initialized from the 3D soil fields produced by the previous week's simulation, allowing continuity of soil status during the whole yearly model run. A systematic validation of calculated meteorological fields was carried out on meteorological datasets collected from some Italian regional meteorological networks (Vitali et al., 2010). Validation results show a satisfactory description for all the considered meteorological variables over coastal and inland plains, which are the main target areas for air quality assessment and management in Italy. The model performance slightly deteriorates over mountainous areas, especially as far as wind fields reconstruction is concerned. This shortcoming is mainly attributable to model resolution, which is insufficient to properly resolve Alpine valleys features and to reproduce sharp mountain or valley measured values.

3.2. Emissions

Emissions of PAHs and other species considered by the two versions of FARM model have been prepared starting from ISPRA and EMEP (MSC–E for PAHs, MSC–W for all other pollutants) inventories, for Italy and for the portion of surrounding countries inside the simulation domain respectively.

EMEP/MSC–E inventory has been developed using official data received from the EMEP Centre on Emission Inventories and Projections (CEIP) (http://www.ceip.at). For countries not reporting their national data, emission totals for 2005 have been

estimated by interpolation between 2000 and 2010 of non–official estimates and projections made by TNO (Van der Gon et al., 2007).

The Italian inventory (hereafter ISPRA2005) has been compiled by ISPRA (National Institute for Environmental Protection and Research, 2009) at the national level, considering sector–specific emission factors and activity data, and then disaggregated at provincial level (NUTS3) using activity–related proxy data (population, industrial product statistics, vehicles fleets and mileages, etc.). The inventory follows the CORINAIR methodology defined by the European Environmental Agency (EEA, 2009), with emission sources classified according to the SNAP scheme (Standard Nomenclature for Air Pollution), allowing an easy identification of the relative contribution of different emission activities. In the inventory emission sources are available as:

• *point sources*: mostly large industrial facilities and energy production plants; these sources are individually characterized with geographical coordinates, physical and thermodynamic parameters (stack height and diameter, gas exit speed and temperature); related emissions are either directly measured or estimated through process–specific emission factors from fuel consumptions or activity levels, accounting also for abatement techniques that can be in place;

• *diffuse sources*: all other sources that cannot be considered on an individual basis and whose activities take place over a larger area; their emissions are usually estimated through statistical data of the underlying activities.

ISPRA2005 dataset contains information on NO_x, SO_2, PM_{10}, CO, NMVOC and the main micro–pollutants. Table 1 reports the percentage contributions of the main groups of activities to Italian PAHs emissions, according to the national inventory: most of the emissions come from domestic heating (about 37%), production processes (about 33%) and waste treatment (about 26%) activities. It has to be noted that the national estimates of wood usage in combustion processes have been recently revised (EEA, 2009), with a portion of the resulting emissions allocated to the waste treatment sector of the inventory, as "burning of residuals from agricultural activities". Due to the uncertainty of the attribution to different sectors, in the modelling application all emissions from biomasses usage have been considered as coming from the residential sector, and modulated in time accordingly. Speciation of total PAHs into B[a]P, B[b]F, B[k]F and I_P has been performed using profiles reported in EEA (2000) and EEA (2009). Profiles for natural mass burning have been derived from Finlayson–Pitts and Pitts (1999). For the modelling application, emission inventories data have then been allocated to the simulation grid using sector–specific spatial proxies (land–use, population, road networks) and modulated in time using typical yearly, weekly and daily profiles of each sector. Point sources from the national inventory have been allocated to vertical grid cells considering the plume rise effect over each stack, computed using hourly meteorological fields.

3.3. Initial, boundary and background concentrations

Initial and boundary conditions (IC/BCs) for FARM air quality model have been derived from continental scale simulation results at 50 km horizontal resolution provided by EMEP models for the year 2005. Three–hourly EMEP/MSC–W concentration fields have been used to assign IC/BCs for the gas and aerosol species used by the two versions of FARM, while six–hourly EMEP/MSC–E results have been used for the four PAHs indicators. O_3, $CH_3C(O)O_2$ and H_2O_2 time varying background concentration fields needed by the simplified version of FARM model have been assigned on hourly basis using the results from a previous simulation (Mircea et al., 2010), performed over the same domain with a version of FARM model implementing the SAPRC90 chemical mechanism (Carter, 1990). The daily cycle of OH concentrations, expressed in (molecules cm^{-3}), has been assigned using the following function depending on the solar zenith angle Z (http://www.emep.int/UniDoc/node9.html):

$$10^4 + 4 \cdot 10^6 \, exp(-0.25/cos Z) \quad day$$
$$10^4 \quad night \tag{8}$$

4. Simulation Results

The analysis of model results has been focused on B[a]P that, according to the Directive 2004/107/EC, should be used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in ambient air. Figure 1 shows the comparison between yearly average B[a]P concentrations in aerosol phase simulated by the two versions of FARM model, ACID–PAHs and SAPRC99–PAHs, and by the EMEP/MSC–E model. The concentration fields produced by the two versions of FARM model exhibit a similar spatial structure, with higher values simulated by the full chemistry version. FARM maps look more spotty and show higher values with respect to EMEP/MSC–E model. This could be due to the higher spatial resolution adopted by the national modelling system both horizontally and in the lowest vertical layers with respect to MSC–E model which has a spatial resolution of 50 km and adopts a P–σ vertical system with the first four levels approximately at 40, 115, 230 and 430 m. As pointed out in Jimenez et al. (2005), the use of a smaller grid size and therefore of a more realistic topography, in conjunction with the assimilation procedure adopted to reconstruct meteorological fields, can have important effects on mesoscale atmospheric flows and consequently on the dispersion of pollutants, enhancing local maxima near area sources. This could be particularly relevant in Po Valley, where the Alps form a barrier at the north of the region. The differences in the north–eastern part of the domain could be due to a combination of the different vertical level structure and vertical allocation of sources (locations and stack parameters of point sources were not available for sources outside Italy). The higher values estimated by FARM over Italy in correspondence with the most populated areas (Milan, Rome and Naples metropolitan areas) and around major industrial sites (coast of Tuscany, Taranto in south–east of the country, Sicily, southern Sardinia) could be ascribed to higher emissions attributed by the national inventory (see Table 2). For B[a]P, total emissions according to the national inventory are 31% higher; for I_P the difference between Italian emissions considered by EMEP (obtained on the basis of Van der Gon et al., 2007) and by the national inventory is even more relevant, and the relative ratios between I_P and other PAHs are significantly lower than those estimated in surrounding.

Table 1. Percentage contributions of different activities to Italian PAHs emissions, according to the national inventory

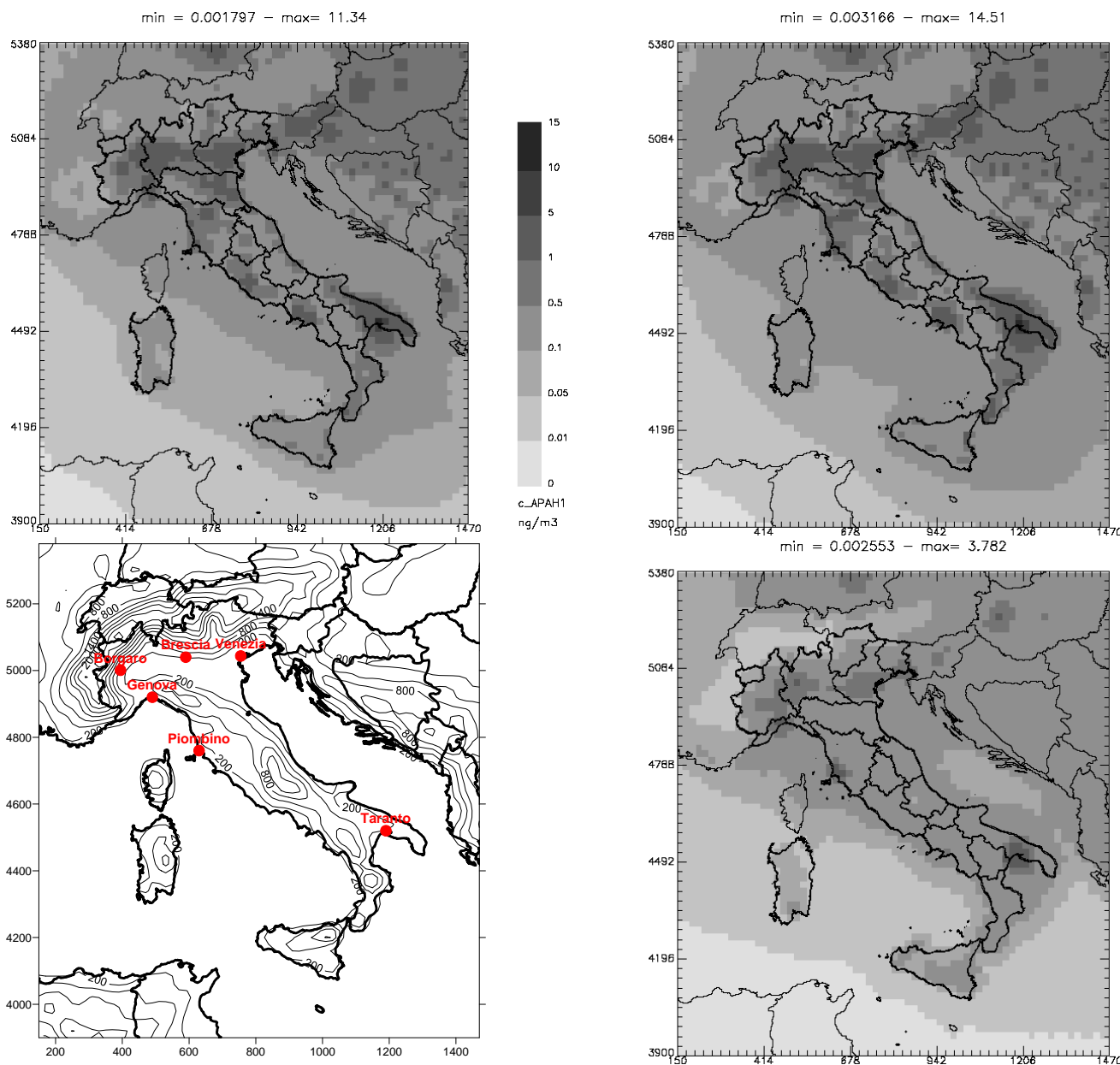| Activity	B[a]P	B[b]F	B[k]F	I_P	PAHs
Energy production	0.2	0.5	0.9	0.4	0.4
Non-industrial combustion	26.9	56.9	59.6	26.4	36.8
Combustion in industry	1.3	3.2	2.4	0.9	1.7
Production processes	43.3	4.3	1.8	53.8	33.2
Road transport	1.1	2.9	4.8	1.6	2.0
Other transport and mobile machinery	0.0	0.4	1.1	0.1	0.3
Waste treatment	27.1	31.8	29.5	16.8	25.6

Figure 1. *Yearly averaged B[a]P concentrations modeled for 2005; top left: ACID-PAHs; top right: SAPRC99-PAHS; bottom right: EMEP (MSC-E); bottom left: topography.*

Table 2. *Italian PAHs emissions (kg year⁻¹), as attributed by the national inventory (ISPRA) and as considered by EMEP/MSC-E model*

Species	ISPRA	EMEP
B[a]P	54 271	41 404
B[b]F	27 874	49 684
B[k]F	15 012	18 628
I_P	35 031	210
Total	132 187	109 925

According to the simulation results, large areas of the Italian territory exceed the target value of 1 ng m^{-3}, with maxima around Taranto (Puglia Region, southern Italy) where operates one of Europe's largest iron and steel plants. Seasonal field campaigns performed during 2004 in winter and summer periods, at sites influenced only by the industrial complex and not by urban or other industrial emissions, have confirmed the high concentrations simulated in this area. Indeed, extremely high levels (up to 65 ng m^{-3}) were recorded during winter periods few kilometres away from the industrial area (Di Filippo et al., 2010).

To evaluate the results of the modelling system over Italy, a comparison between computed and measured B[a]P concentrations at monitoring stations has been performed. Since the current national air quality database (BRACE, http://www.brace.sinanet.apat.it) contains very limited information for the year 2005, further information was requested to the Regional Environment Protection Agencies. The collected observations have different time resolutions (daily or monthly) and often cover only short periods of time. According to the European Directive 2008/50/CE, only the stations fulfilling the time coverage requirements have been actually considered (33% for fixed sites and 14% for indicative measurements). Moreover, due to the spatial resolution of the simulation, the comparison has been focused on the stations classified as "background", which should be less affected by sources in the near range. The stations that fulfilled the above criteria (see the SM, Figure S1) are mostly located in the Po Valley, mainly in Piedmont region, except for the Cinecittà background station, located in Rome (central Italy, not shown in the figure). Since daily data were generally not available, monthly averages have been computed for both observed and computed concentrations, excluding from the analysis days with

Table 3. *Statistical analysis over monthly averaged B[a]P concentrations over Piedmont region*

Metric		Range	Units	Observations	FARM Full	FARM Simplified	EMEP (MSC-E)
Average	$\overline{P} = \frac{1}{N}\sum_{i=1}^{N} P_i$		(ng m^{-3})	0.99	1.29	1.21	0.48
Standard var.	$\sigma_p = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(P_i - \overline{P}\right)^2}$		(ng m^{-3})	1.26	1.39	1.42	0.34
Correlation	$R = \dfrac{\frac{1}{N}\sum_{i=1}^{N}\left(P_i - \overline{P}\right)\cdot\left(O_i - \overline{O}\right)}{\sigma_P \sigma_O}$	-1 to +1	(-)		0.78	0.79	0.56
Factor of 2	$FAC2 = \left(\frac{1}{N}\sum_{i=1}^{N} i \,/\, \left(0.5 \leq \frac{P_i}{O_i} \leq 2\right)\right)\cdot 100$	0 to +100%	(%)		46.5	46.5	35.2
Mean Fractional Bias	$MFB = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(P_i - O_i\right)}{\left(\frac{P_i + O_i}{2}\right)}\cdot 100$	-200 to +200%	(%)		8.0	0.4	-4.8
Mean Fractional Error	$MFE = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|P_i - O_i\right|}{\left(\frac{P_i + O_i}{2}\right)}\cdot 100$	0 to +200%	(%)		18.5	19.3	20.1

missing observations. The comparison between observed and computed B[a]P monthly concentrations, reported in Figure S2 (see the SM), evidences the capability of the national modelling system to capture the seasonal behaviour of this pollutant, with differences between winter and summer values spanning over more than one order of magnitude. This is presumably the result of a strong yearly cycle in emissions, linked to the usage of wood for residential heating, enhanced by lower dispersion in wintertime, the typical condition experienced in the Po Valley. The importance of combustion in the residential sector has also been confirmed by the source apportionment study presented in the following Section. It is interesting to note that despite the differences in the treatment of chemical processes, the two versions of FARM model produce similar results, confirming the validity of the approach adopted in the simplified version. Under/overestimations evidenced by such comparison may be more connected to uncertainties in emission data, reproduction of meteorological and chemical conditions of the atmosphere that may be improved by increasing the horizontal spatial resolution of the simulations. Also, the quality of the data, such as the irregular variability of monthly measured values may be another source of discrepancy. On the other side, corresponding monthly averages provided by EMEP model generally tend to underestimate observed levels and show a less pronounced seasonal variation.

To further evaluate the performance of the two versions of FARM model, a statistical analysis has been performed, considering only Piedmont Region sites (i.e. excluding Venezia–Mestre and Cinecitta stations) to have a more homogeneous set of monitoring stations, although on a smaller area. The results, summarized in Table 3, show a good performance of the two versions of FARM model according to the Pearson Correlation Coefficient (R) and the fraction of modelled values within a factor of two of observations (FAC2), scoring near 50% for both versions; index values are higher than the corresponding ones for EMEP model. The FARM version with simplified chemistry shows almost no bias, while the version with full chemistry exhibits a slight overestimation and the EMEP model a slight underestimation, consistently with the values of the overall averages; the Mean Fractional Error is otherwise relatively stable among the different models.

5. Source Apportionment

To better understand the influence of different sources on B[a]P concentrations in different parts of the country, a quantitative source apportionment has been performed. This analysis has been carried out using the simplified version of FARM model that, while performing similarly to the full chemistry version, has the advantage to be far less computationally expensive. The methodology used for this evaluation is based on the so–called "brute force" method (Koo et al., 2009; Burr and

Zhang, 2011), that consists on multiple sensitivity runs of the air quality model, each one of them performed varying the emissions from sources of interest. The contribution of a given group of sources is then estimated by comparing the results of the corresponding sensitivity run with those obtained with a reference run, where the full set of sources is completely active. The sensitivity runs have been performed for two months, January and July, representative of winter and summer conditions, respectively. The results are given in terms of maps showing absolute (ng m^{-3}) and relative (percentages) contributions to average B[a]P concentrations. Relative contribution maps are useful to give an insight on the fraction of B[a]P that can be attributed to different groups of sources or to foreign emissions while absolute maps allow to estimate the actual impact of these sources on B[a]P concentrations at a given location (See Figures S3, S5 and S6 in the SM).

5.1. Foreign sources

The contribution of emissions outside Italy to B[a]P average concentrations on grid points located inside the country is shown in Figure S3 (see the SM). This has been evaluated through a sensitivity run with boundary conditions and emissions outside Italy zeroed out, keeping for background species the same concentrations of the reference run. Then, the contribution of foreign sources has been estimated at each grid point as:

$$100 \times (C_{ref} - C_s)/C_{ref} \qquad (9)$$

where C_{ref} is the concentration of the reference run and C_s is the concentration of the sensitivity run, averaged over each month. The maps in Figure S3 evidence that the foreign sources have a weak influence on B[a]P concentrations; the contribution of their emissions is larger near the land border at the north, over the major islands (Sardinia and Sicily) and at rural areas in the central–southern part of the Italian peninsula, far from densely inhabited areas (see the SM, Figure S3). Contributions from foreign emissions are generally larger during summer than during winter; this behaviour is explained by the high influence of national emissions from wood combustion, used for the heating of buildings in wintertime, as discussed in the following section.

5.2. Sector contributions

After the foreign sources apportionment, the contribution from national sources has then been further split according to the main sectors of anthropic activities. For each sector, national emissions from the corresponding sources have been reduced by a fixed factor, chosen equal to −20% in order to highlight the contributions without heavily modifying the local chemical regime.

Table 4. *Seasonal modeled contributions (%) from different sectors to the B[a]P concentrations at different locations (contributions below 0.1% are considered not significant, and indicated as "n.s."). See Figure 1 for the location of the sites*

Month	Sector	Location					
		Borgaro	Venezia Mestre	Brescia	Genova	Piombino	Taranto
January	Energy production	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	Non-industrial comb.	97.2	97.0	86.1	64.2	54.2	21.8
	Industry	2.1	2.0	12.5	35.2	45.5	78.1
	Road transport	0.6	0.7	1.1	0.5	0.2	0.1
	Waste	n.s.	0.1	0.2	n.s.	n.s.	n.s.
	Other	n.s.	0.1	n.s.	n.s.	n.s.	n.s.
July	Energy production	0.4	5.4	0.1	n.s.	0.1	n.s.
	Non-industrial comb.	44.8	53.7	13.3	0.7	0.4	0.1
	Industry	47.4	26.1	82.3	99.1	99.5	99.9
	Road transport	7.1	9.4	3.7	0.1	n.s.	n.s.
	Waste	n.s.	4.3	0.4	n.s.	n.s.	n.s.
	Other	0.3	1.1	0.1	n.s.	n.s.	n.s.

As done for the foreign contribution, concentrations of background species have been assigned as in the reference run. After running the air quality model, the variation of average concentration with respect to the reference run in each grid point has been calculated as $\Delta_i = C_{ref} - C_i$, where i stands for one of the sectors. The procedure has then been repeated for all sectors, and at the end the relative contribution of each has been calculated, at each grid point, as the ratio between the single variation Δ_i and the sum of all of them, expressed as percentage:

$$100 \times \Delta_i \big/ \Sigma_i \Delta_i \qquad (10)$$

The sectors in which the activities were grouped ("macrosectors") are:

- combustion in energy production and transformation,
- non–industrial combustion (residential and commercial),
- combustion in manufacturing industry,
- industrial processes,
- road transport,
- other mobile sources,
- waste treatment and disposal.

To help the interpretation of the results, Figure S4 (see the SM) shows the distribution of PAH emissions at provincial level, the location and magnitude of point sources and the contribution of different macrosectors to provincial emissions. The maps of resulting contributions from the most influencing sectors during the months of January and July are reported in Figures S5 and S6, while the seasonal contributions at selected sites (see Figure 1 for their locations) are reported in Table 4. The results show that, almost everywhere over the Italian territory, B[a]P concentrations are overwhelmingly determined by emissions from non–industrial combustion, for which the main fuel is wood (as previously stated, all emissions from wood usage contained in the national inventory have been accounted for as coming from the residential and commercial sector). The dominance of this sector at Borgaro and Venezia Mestre (Table 4) explains the strong seasonal variability observed in the monitoring data collected at those locations (see the SM, Figure S2). In absolute terms, the location of the largest contributions from non–industrial combustion reflects the distribution of the densely populated areas. Important exceptions are visible close to major industrial areas near the cities of Genova, Trieste, Piombino (on the coast of Tuscany) and Taranto, in the Brescia area (central part of northern Italy) and North–eastern Sardinia. In these locations industrial activites give a quite relevant contribution, or even the dominant one, also during winter season (see Table 4). The largest absolute contribution from industrial processes is found in Taranto, whose steel industries are the largest individual sources of PAH in the country according to the

inventory. The contribution of industrial processes with respect to other sectors becomes more important in summertime, when non–industrial combustion is substantially lower, although total concentrations are substantially lower than in wintertime. Road traffic (not shown in the maps) contributes for a few percentage points, with highest absolute contributions in the Po Valley and near Rome and Naples metropolitan areas. The remaining sectors play an almost negligible role.

6. Conclusions

Two versions of FARM model, implementing respectively simplified gas–phase chemical mechanisms for sulphur and nitrogen compounds coupled with a bulk aerosol module (ACID–PAHs) and the SAPRC99 gas phase mechanism interfaced with *aero3* aerosol module (SAPRC99–PAHs) have been extended in order to take into account partitioning mechanisms of PAHs between gaseous and particulate phases. These versions of the model have been run for the year 2005 over Italy in order to reconstruct B[a]P concentrations in aerosol particles. The simulations have been performed using emission data from national and European inventories and boundary conditions provided by EMEP continental scale models (MSC–E and MSC–W). The analysis of model results has then been focused on B[a]P, used as a marker substance for PAHs. The spatial distribution of B[a]P yearly average concentrations, simulated with the national modelling system at 20 km horizontal resolution, showed larger values than EMEP/MSC–E simulation, particularly at areas characterised by significant urban and industrial emissions. This could be the result of the combined role played by greater emissions in the national inventory and by the higher resolution adopted by the national scale modelling system. Moreover, the effects induced by the use of higher resolution topography could play a relevant role on the meteorological fields and thus on the dispersion of pollutants.

Modelled concentrations have been then compared with available observations, focusing on "background" sites less affected by sources in the near range and more appropriate for the spatial resolution adopted in the simulations. Due to the scarcity of experimental data for the year 2005, the analysis has been limited to a set of stations located in the Po Valley and one urban background station located in Rome. The comparison between observed and predicted monthly levels has evidenced the capability of the two versions of FARM to capture the seasonal behaviour of B[a]P characterised by higher values during winter. The comparison has also evidenced a good reproduction of the spatial distribution and temporal variability of concentrations at stations, with some exceptions possibly due to the adopted model resolution, uncertainties in emission inventories and measurements representativeness. The statistical analysis shows

comparable performances for the two versions of the FARM model and better results than those provided by the continental scale EMEP/MSC–E model.

Given the similarity of the results obtained with ACID–PAHs and SAPRC99–PAHs, a quantitative source apportionment has been carried out, using the simplified version of FARM model, to estimate the influence of different sources to B[a]P concentrations in different parts of the country. This analysis shows that the effect of foreign emissions is higher in the areas near the Alpine border at the north, over the major islands (Sardinia and Sicily) and in some rural areas in the central–southern part of the Italian peninsula, far from densely inhabited areas. According to these simulations, the foreign emissions contribute to B[a]P concentrations more during winter than during summer. Concentrations from 0.1 to 0.3 ng m^{-3} are constantly added to the local pollution over the whole Italy during winter; during summer the contribution is mostly between 0.01 to 0.05 ng m^{-3}.

B[a]P concentrations seem to be determined almost everywhere over the country by national emissions coming from residential heating, particularly where wood burning devices are used. The contribution of the industrial sector becomes relevant around major facilities, with the largest absolute contribution in Taranto, whose steel industries are the largest individual source of PAHs in the country according to the national emission inventory. Road traffic contributes for a few percentage points, with highest absolute contributions in the Po Valley and near Rome and Naples metropolitan areas. The remaining sectors play an almost negligible role.

Although giving a first insight on the relationships among B[a]P concentration distribution and sources location within different parts of the country, this study could benefit of an extension to more recent years. Some Italian regional environmental agencies, in charge of routine air quality monitoring, are in fact increasing their observational capabilities on PAHs. The availability of a wider set of reliable observations, covering different parts of the country, could improve our knowledge on the fate of these pollutants and will allow a wider evaluation of model results.

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Supporting Material Available

FARM description (S1); Precipitation scavenging module (S2); in–cloud (W_{in}) and sub–cloud (W_{sub}) scavenging ratios and collection efficiencies ($\overline{E}$) used in precipitation scavenging calculation for PAHs (Table S1); location of B[a]P background monitoring stations for year 2005 (Figure S1); observed and computed monthly variations of B[a]P concentrations at background monitoring stations (Figure S2); spatial distribution of contributions from non–Italian sources to the average concentrations of B[a]P in January and July (Figure S3); PAHs National emission inventory for year 2005 (Figure S4); spatial distribution of main contributions from activity sectors to the average concentrations of B[a]P in January (Figure S5); spatial distribution of main contributions from activity sectors to the average concentrations of B[a]P in July (Figure S6). This information is available free of charge via Internet at http://www.atmospolres.com.

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