Can biomonitors effectively detect airborne benzo[a]pyrene? An evaluation approach using modelling~~Can we use modelling methodologies to assess airborne benzo[a]pyrene from biomonitors? A comprehensive evaluation approach~~

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Abstract

Biomonitoring data available on levels of atmospheric polycyclic aromatic hydrocarbons (PAHs) in pine needles from the Iberian Peninsula was used to estimate air concentrations of benzo[*a*]pyrene (BaP) and, at the same time, fuelled the comparison with chemistry transport model representations. Simulations with the modelling system WRF+EMEP+CHIMERE were validated against data from the European Monitoring and Evaluation Programme (EMEP) air sampling network and using modelled atmospheric concentrations as a consistent reference in order to compare the performance of vegetation-to-air estimating methods. A spatial and temporal resolution of 9 km and 1 hour was implemented. The field-based database relied on a pine needles sampling scheme comprising 33 sites in Portugal and 37 sites in Spain complemented with the BaP measurements available from the EMEP sites. The ability of pine needles to act as biomonitoring markers for the atmospheric concentrations of BaP was estimated converting the levels obtained in pine needles into air concentrations by six different approaches, one of them presenting realistic concentrations when compared to

the modelled atmospheric values. The justification for this study is the gaps still existing in the knowledge of the life cycles of semi-volatile organic compounds (SVOCs), particularly the partition processes between air and vegetation. The strategy followed in this work allows the effective ~~definition~~ estimation ~~of the transport patterns (e.g. dispersion) established~~ by the model ~~for~~ of concentrations in air and vegetation and of the best approaches to estimate atmospheric levels from ~~concentrations and the estimated~~ values found in vegetation.

1 Introduction

Semi-volatile organic compounds (SVOCs) are widespread chemicals that even at low concentrations possess carcinogenic capacity (Baussant et al., 2001) and ecotoxicity (Solé, 2000) due to their persistence in different environmental matrices (air, soil, water, living organisms). In particular, polycyclic aromatic hydrocarbons (PAHs) are originated by natural and anthropogenic combustion processes or released from fossil fuels (Mastral and Callén, 2000) and can be transported in the atmosphere over long distances in gaseous phase or as particulate matter (Baek et al., 1991). The lighter PAHs (2 or 3 aromatic rings) exist mainly in the former, whereas the heavier (5 to 6 rings) consist almost entirely of the latter (Bidleman, 1988), and this is the case of 5-ringed benzo[*a*]pyrene (BaP), arguably the most studied PAH. BaP is the reference for PAH air quality standards, as defined by the European Commission (Directive 2008/50/EC), which sets a limit of 1 ng m^{-3} over a 1-year averaging period (European Commission, 2008).

The establishment of strategies for sampling and modelling of SVOCs in the atmosphere aiming at the definition and validation of their spatial, temporal and chemical transport patterns can be achieved by an integrated system of third-generation models that represent the current state of knowledge in air quality modelling and experimental data collected in field campaigns (Jiménez-Guerrero et al., 2008; Morville et al., 2011). The modelling methods currently applied for SVOCs use very simple mass balance techniques or have deterministic approaches, reflecting the complexity to characterise adequately the chemical transport processes. These limitations urge for more experimentally-based information, hence the need to combine field-based campaigns and modelling to address the problem properly (Jakeman et al., 2006), including multi-matrix approaches whenever possible.

Moreover, measurements of pollutants such as PAHs are labour-intensive compared to those of criteria air contaminants such as ozone and particulate matter, and the processes governing their atmospheric fate and representation within chemistry transport models (CTMs) are not yet well understood (Galarneau et al., 2013), particularly in terms of uncertainties associated with the emissions and re-emissions from sinks, partition patterns, volatility and fate of SVOCs, among others. A number of atmospheric modelling studies have tried to characterise the levels and spatial-temporal patterns of PAHs (most of them focusing on BaP) using CTMs both on global (Sehili and Lammel, 2007; Lammel et al., 2009; Friedman and Selin, 2012) and regional scales (Matthias et al., 2009; Aulinger et al., 2011; Bieser et al., 2012;

San José et al., 2013). These authors identify a lack of measurement data in Europe to evaluate the behaviour of the CTMs against observations. For example, Bieser et al. (2012) use only six European Monitoring and Evaluation Programme (EMEP) stations (four in the Scandinavian region) and six additional sites in Germany and the UK to evaluate their year 2000 simulations. Bernalte et al. (2012) also highlight the importance of studies on PAHs over the Western Mediterranean (Iberian Peninsula) in order to increase the knowledge of the ambient levels in this region. For that purpose, San José et al. (2013) conducted a 12-week modelling study supported by a field campaign to describe the behaviour of their WRF+CMAQ simulations, but using only a single location in Spain.

Hence, there is a strong need to have trustful information on the atmospheric levels of compounds like BaP and other SVOCs, in particular in areas with limited information, like over the Iberian Peninsula. In that sense, vegetation species can play a decisive role as biomonitors of the incidence and chemical transport of atmospheric pollutants (Maddalena et al., 2003). Coniferous trees are particularly important, given their worldwide distribution and specific characteristics. However, even if some studies report geographical or temporal patterns of PAHs in coniferous needles (Weiss et al., 2000; Hwang and Wade, 2008; Lehndorff and Schwark, 2009; Augusto et al., 2010; Ratola et al., 2010; Amigo et al., 2011; Ratola et al., 2012) only a few deal with their air-vegetation distribution (St-Amand et al., 2009a; 2009b). In addition, to our knowledge there is no study regarding the simultaneous use of field and modelling data to assess the distribution of PAHs between air and pine needles. Consequently, if trustful estimates of the atmospheric incidence could be obtained from vegetation, the abundance of biomonitors such as pine needles would provide essential information about the regional and global atmospheric behaviour of persistent contaminants.

Under these premises, the WRF+CHIMERE modelling system, coupled to BaP emission data from EMEP was run and evaluated for the Iberian Peninsula. The modelled depositions were compared to data from biomonitoring campaigns carried out along 70 sites, to assess the ability of the model to reproduce BaP canopy deposition. Monitoring data from EMEP (Torseth et al., 2012) was used to validate the modelled atmospheric BaP climatologies (2006-2010). A total of six approaches were tested to estimate the conversion of BaP levels from vegetation into air. To achieve this, the atmospheric levels from these approaches were evaluated against the modelled air concentrations.

2 Experimental section

2.1 Pine needles sampling

The Iberian Peninsula, located in the SW of Europe, has an area close to 600,000 km^2 and a population of almost 60 million, the majority of which distributed along the Atlantic and Mediterranean coastlines, except for some important conurbations such as Madrid, Seville or Zaragoza. Forests (with several pine species commonly present) are scattered through the whole territory. Mountainous areas follow the same trend, with the most elevated chains found in the Northern borders (Pyrenees and Cantabria) and in the south (Sierra Nevada). Rural activities can be found almost everywhere, but are particularly important for the economy in the central plateau, where population density is scarcer. A representation of the different land uses in the target domain as represented by the WRF+CHIMERE modelling system can be found in Ratola and Jiménez-Guerrero (2015). ~~(but with a clear predominance in the north half) and several pine species are commonly present.~~ In this study, and according to their availability, needles from *Pinus pinaster*, *Pinus pinea*, *Pinus halepensis* and *Pinus nigra* with up to 1.5 years of exposure to contamination were collected from the bottom and outer branches, placed in sealed plastic bags, kept from light and frozen until extraction. The sampling campaigns were carried out in 33 sites in Portugal and 37 in Spain, in both cases including urban, industrial and rural or remote areas. For further description of these campaigns, the reader is referred to Ratola et al. (2009; 2012).

2.2 Pine needles analysis and quantification

The analytical procedure used to quantify the levels of PAHs (BaP included) in pine needles was reported previously (Ratola et al., 2009; 2012). A brief description of the methodology and of some characteristics of the pine needles from the different species can be found in Supporting Information.

2.3 Methods for the estimation of BaP air concentrations from vegetation.

Given the lack of information on atmospheric concentrations of BaP in the sampling sites chosen for this study, an estimation of those values from data provided by biomonitoring studies with vegetation (coniferous needles in this case) was required. Resorting to literature, six approaches (four of them using the same main calculation method, varying only one parameter) were tried and the resulting estimated BaP concentrations compared with the modelling experiments.

Approach 1a. This approach is based on the studies by St. Amand and co-workers (2007; 2009a; 2009b), who measured the levels of PBDEs and PAHs in vegetation (Norway spruce needles in this case) and in the surrounding atmosphere (both gas-phase and particulate material) and presented a strategy to estimate the air concentrations from those in vegetation and vice-versa. In brief, the atmospheric concentration of SVOCs (Ca) estimated from the levels in vegetation can be determined by the contribution of particle-bound (Cp) and gaseous (Cg) phases. In the case of BaP, being a high molecular weight PAH, the gas-phase contribution is negligible, which means ø (ratio between particle and particle+gas phases) ≈ 1 and Ca can be given by:

Ca = Cp ~~+ Cg~~ ~~(1) with~~

~~Cp~~ = (Cvp*m) / (A*v_p*t) (~~2~~1) ~~and~~

~~Cg = (Cvg*m) / (A*v_{gt}*t) (3)~~

where Cvp~~, Cvg~~ - contribution of particle-bound~~ and gaseous~~ deposition processes to the total concentration in vegetation~~, respectively~~ (ng g^{-1}); m - dry weight of pine needles (g); A - total surface area (m^2) of vegetation (in our study, pine needles); v_p - particle-bound deposition velocity (m h^{-1}); ~~v_{gt} – net gaseous transfer velocity (m h^{-1});~~ t – environmental exposure time of pine needles (h) with Cp~~ and Cg~~ expressed in ng m^{-3}. ~~In the case of BaP, being a high molecular volume PAH, the gas-phase contribution is negligible, which means ø (ratio between particle and particle+gas phases) ≈ 1 and that v_p can be calculated directly by equation 2. However, s~~Since it was impossible to calculate v_p for our samples, due to the lack of information on the atmospheric concentrations, in this first approach the value calculated by St. Amand et al. (2009a) for Norway spruce (*Picea abies*) needles was used: 10.8 m h^{-1}. Values of the mass and total surface area for the pine needles studied are presented in Table S1. The exposure time was estimated considering that the new needles sprung out on April 15 and counting the hours from this day to the sampling date.

Approaches 1b, **1c and 1d.** These approaches follow the same strategy, only with different v_p values calculated from studies in literature reporting BaP concentrations in air and pine needles (from *Pinus sylvestris* trees in cases 1b and 1c and a coniferous forest in 1d). Approach 1b refers to the work by Klánová et al. (2009) and the estimated v_p (BaP) is 0.0039 m h^{-1}, while approach 1c comes from the work by Tremolada et al. (1996), with v_p (BaP) =

0.0263 m h^{-1}. For the 1d approach, it was considered the deposition velocity Horstmann and McLachlan (1998) found for BaP over a coniferous forest canopy: 2.196 m h^{-1}. As can be seen, the variability of v_p is evident, not only considering different species of vegetation, but also using the same species in different locations. In the case of approaches 1b and 1c, Klánová et al. (2009) sampled remote areas whereas Tremolada et al. (1996) considered more urbanised locations, which may justify the higher deposition velocity in the latter case. Differences in the uptake of PAH by different pine species in the same sampling sites are also described in literature (Piccardo et al., 2005; Ratola et al., 2011).

Approach 2. This approach follows the work of Tomashuk (2010), which used biomonitoring results in *Pinus nigra* needles and in turn profits from a study by Simonich and Hites (1994). In the latter, an air-vegetation partition coefficient (Kv) is defined by:

l~~L~~n Kv = (1000/T)*slope – 35.95 (~~4~~2)

with T – air temperature (K); slope – calculated by Simonich and Hites (1994) for some PAHs. And from Kv, the air concentration of PAHs (Ca) can be estimated by (in ng m^{-3}):

Ca = Cv / (Kv*lipid) (~~5~~3)

with Cv – concentration in the vegetation (ng g^{-1}, dw); lipid – lipid content per dry weight of pine needles (mg g^{-1}, dw). Values of the lipid content for the pine needles studied are presented in Table S1.

Approach 3. Chun (2011) measured PAH concentrations in *Pinus koraiensis* needles and the surrounding air and came up with the following correlation between log K_{oa} and Cv/Ca:

From acenaphthylene to chrysene:

Ca = Cv / exp [(log K_{oa} – 7.9603) / 0.4557]~~= 0.4557*ln (Cv/Ca) + 7.9603~~ (~~6~~4)

with Ca – concentration in air (ng m^{-3}, dw); Cv – concentration in the vegetation (ng/g, dw)~~;~~ ~~Ca – concentration in air (ng m^{-3}, dw)~~

From chrysene to benzo(ghi)perylene (the equation used to calculate BaP concentrations):

Ca = Cv / exp [(log K_{oa} – 12.18) / (-0.2272)]~~log K_{oa} = -0.2272*ln (Cv/Ca) + 12.18~~ (~~7~~5)

~~Log~~ log K_{oa} is a temperature-dependent coefficient, and was calculated using the following equation:

$$\log K_{oa} = A + (B/T) \qquad (\cancel{8}6)$$

where coefficients A and B are given by Odabasi et al. (2006) and the temperature (T) in each site was the mean from the three months previous to sample collection, since it corresponded to the intervals of exposure between campaigns (with a seasonal periodicity for most sampling points). The equilibrium between air and pine needles is still not completely understood and can be a slow process for compounds with high log Koa such as BaP (Mackay, 1991) and it may not be possible to acknowledge if “non-equilibrium” conditions or alternative processes (Tremolada et al., 1996).

2.4 Modelling experiment and validation

In this study, the Weather Research and Forecasting (WRF) (Skamarock et al., 2008) and the CHIMERE modelling system (Menut et al., 2013), with a resolution of 9 km for the entire Iberian Peninsula coupled to EMEP BaP emissions (Vestreng et al., 2009), was run and evaluated for the Iberian Peninsula in a simulation covering the years 2006 to 2010 on an hourly basis. This CHIMERE version has been modified to include gaseous and particulate BaP. Gas-phase degradation by OH radicals, which represents over 99% of the degradation path for gas-phase BaP, was accounted for, with a $k_{OH} = 5.68 \times 10^{-11}$ (Schwarzenback et al., 2003). But more importantly, the oxidation of particulate BaP with ozone was also included, since the respective reaction rate is one order of magnitude higher than other degradation processes, and can be considered the only effective degradation path for particulate BaP in the atmosphere (Bieser et al., 2012). In this case, the reaction constant follows the approach of Pöschl et al. (2001):

$$k = k_{max}\,[O_3]/(1 + K_{O3}[O_3]) \qquad (7)$$

being $k_{max} = 0.015$ s^{-1} and $K_{O3} = 2.8 \times 10^{-13}$ cm^3.~~This CHIMERE version includes gaseous and particulate BaP and its degradation by OH radicals, which represents over 99% of the degradation path for BaP~~. A bias ~~correction~~ adjustment technique was applied and is referred in Supporting Information, together with a description of the modelling set-up and validation procedures (Table S2). All modelled concentrations presented in this work are bias-adjusted.

The BaP concentrations in pine needles used in this work are taken from biomonitoring campaigns previously performed in the Iberian Peninsula (Ratola et al., 2009; 2010; 2012). These data were compared to the deposition over vegetal canopies as estimated by the

CHIMERE transport model. The dry deposition flux in CHIMERE is directly proportional to the local concentration C of the target compound (in this case, BaP):

$$F = -v_d \times C \tag{8}$$

where F represents the vertical dry deposition flux, the amount of material depositing to a unit surface area per unit time. The proportional constant between flux and concentration, v_d, is known as the deposition velocity. The main factors governing dry deposition are the grade of the atmospheric turbulence, the chemical properties of the species, and the nature of the soil and the vegetation.

The deposition over vegetal canopies in CHIMERE for particles employs a resistance scheme (Wesely, 1989). The dry deposition velocity follows the formulation of Seinfeld and Pandis (1997):

$$v_d = (1/(r_a + r_b + r_a \times r_b \times v_s)) + v_s \tag{9}$$

where r_a is the aerodynamic resistance (or aerodynamic drag) and r_b the resistance at the quasi-laminar sublayer. The aerodynamics resistance is calculated as the integral of the inverse of the diffusivity coefficient K_z up to the middle of the model surface layer, which can be estimated using the analytical formulae of the surface-layer similarity profiles for K (Seinfeld and Pandis, 1997) and v_s stands for the sedimentation velocity. For vegetal canopies, as in our case, corrections have been implemented. These corrections are not detailed in the CHIMERE manual (http://www.lmd.polytechnique.fr/chimere/), but rather supported on the literature presented (Giorgi, 1986; Peters and Eiden, 1992; Zhang et al., 2001). For this reason, and for the sake of brevity, the same strategy is adopted here and readers are referred to those works for further details.

3 Results and discussion

3.1 Model evaluation for vegetation and air levels

The model climatologies for BaP in canopy deposition and air concentration were done under the premise of constituting a base for a broad spectrum of studies within the air-vegetation interactions. In fact, a description of these simulations was mentioned previously by Ratola and Jiménez-Guerrero (2015). However, given the importance for the current study, a summary is presented here, also considering a different perspective.

3.1.1 Vegetation

~~The BaP concentrations in pine needles used in this work are taken from biomonitoring campaigns previously performed in the Iberian Peninsula (Ratola et al., 2009; 2010; 2012). These data were compared to the deposition over vegetal canopies as estimated by the CHIMERE transport model. The dry deposition flux in CHIMERE is directly proportional to the local concentration C of the target compound (in this case, BaP):~~

~~$F = -v_d \times C$ (9)~~

~~where F represents the vertical dry deposition flux, the amount of material depositing to a unit surface area per unit time. The proportional constant between flux and concentration, v_d, is known as the deposition velocity. The main factors governing dry deposition are the grade of the atmospheric turbulence, the chemical properties of the species, and the nature of the soil and the vegetation.~~

~~The deposition over vegetal canopies in CHIMERE for particles employs a resistance scheme (Wesely, 1989). The dry deposition velocity follows the formulation of Seinfeld and Pandis (1997):~~

~~$v_d = (1/(r_a + r_b + r_a \times r_b \times v_s)) + v_s$ (10)~~

~~where r_a is the aerodynamic resistance (or aerodynamic drag) and r_b the resistance at the quasi-laminar sublayer. The aerodynamics resistance is calculated as the integral of the inverse of the diffusivity coefficient K_z up to the middle of the model surface layer, which can be estimated using the analytical formulae of the surface-layer similarity profiles for K (Seinfeld and Pandis, 1997) and v_s stands for the sedimentation velocity. For vegetal canopies, as in our case, corrections have been implemented (Giorgi, 1986; Peters and Eiden, 1992; Zhang et al., 2001).~~

The modelled deposition over vegetal canopies was evaluated against observations compiled from pine needles. Thus, the adequacy of the model's deposition velocity for the Iberian Peninsula is assessed by a direct evaluation of the deposition velocity against observations. This information is summarised in Table 1 and a point-to-point comparison is shown in Supporting Information (Table S3). The samples were explicitly compared with the model period corresponding to their effective exposure interval. Given the assumption that there is a full uptake by the pine needles of the deposited BaP, the modelled deposition flux is converted to pine needles concentration multiplying it by the respective time of exposure (equivalent for the model and the pine needles). The results indicate an overall good ability of the model to reproduce the vegetation's uptake of BaP, when compared to the biomonitors. Generally, the modelled concentrations tend~~s~~ to be overpredicted ~~the concentrations during~~ DJF, MAM and SON, when the deposited BaP is overestimated by 0.08 to 0.17 ng g^{-1} (MFB up to +17%). On the other hand, in summer (JJA) the model is likely to underpredict the measured levels in vegetation (-0.41 ng g^{-1}, -39% as MFB), seemingly due to its tendency volatilise SVOCs as a result of the high temperatures simulated over the Iberian Peninsula. The RMSE remains under 1.5 ng g^{-1} in all seasons (Table 1), indicating a close approach of the model to the levels obtained in pine needles. Particularly noticeable is the accurate reproduction of the spatial patterns. In fact, the estimates from the spatial correlation coefficient (which is highest for MAM and lowest for SON, ranging from 0.77 to 0.87 for all seasons) indicate that regardless of the model bias, the spatial reproducibility of the deposition patterns over the Iberian Peninsula is very well reproduced in all seasons, capturing also the seasonal distribution.

In terms of the modelled levels in canopies, Figure 1 shows that the deposition of BaP are clearly lowest for JJA (under 3 ng g^{-1} over most of the Iberian Peninsula) and have the highest values in DJF and MAM (10-20 ng g^{-1} over north-western Iberian Peninsula and the Cantabria coast). But apart from the geographic distribution being closely related to the emitting areas, the differences in the entrapment of PAHs by the different land uses can play an equally significant role, as observed in the spatial uptake patterns shown in Figure 1. Even if a discussion on the role of the different pine species is beyond the scope of this work, several points were brought to our attention. For instance, it was shown previously that *P. pinaster* needles have a superior uptake capacity towards PAHs than *P. pinea* (Ratola et al., 2011) or *P. nigra* ones (Piccardo et al., 2005). The first two species have a strong implantation in the forests of the Iberian Peninsula, but while *P. pinea* is more equally distributed (although mainly present in the south and Mediterranean coast), *P. pinaster* prevails in the north-west and Atlantic coast. This may be the reason why the model tends to present higher deviations over the northernmost biomonitoring points (*P. pinaster*, MFB = 21%) than over eastern-southern areas, with predominant *P. pinea* (MFB = -17%), as shown in Table S3 of the Supporting Information). It was also suggested that leaf surface properties are more a function of the environmental exposure than of the plant response (Cape et al., 1989). Given all these facts, both chemistry transport models and other parameterisations face a huge task to represent the levels of pollutants in vegetation. In this sense, enhancing the field experimental work on the uptake of these chemicals would be strongly beneficial.

3.1.2 BaP air climatology

As mentioned previously, studies in literature regarding the field monitoring of PAHs levels in the Iberian Peninsula's vegetation are limited and, therefore, modelling strategies can represent a valuable tool to assess BaP levels over the target region. The few existing studies (described in Introduction) reflect two main points: the influence of local sources and the variability of the uptake abilities of the different vegetation species.

Since the main focus of this work is on the climatologies of the atmospheric BaP levels, in order to assess the correct reproducibility of their spatial-temporal patterns the WRF+CHIMERE BaP modelled concentrations were evaluated against EMEP air quality data after the bias ~~removal~~ adjustment explained in the ~~methodology~~ Supporting Information~~section~~.

According to Ratola and Jiménez-Guerrero (2015), the modelled atmospheric concentrations of BaP present normalised biases that are under 30% over all the EMEP stations in the Iberian Peninsula. The fact that both positive and negative biases were found for annual mean concentrations indicates that the model is not generally inclined towards overprediction or underpredicion for all the domain of study. As depicted in Figure 2, the deviations only range between +1.63 pg m^{-3} over the northern Iberian Plateau (Peñausende station, close to the Spanish-Portuguese border) and -4.59 pg m^{-3} (San Pablo de los Montes station, in the southern-central Iberian Plateau). The low biases obtained indicate that the model is reproducing accurately the atmospheric concentrations of BaP, and therefore can be used as a reference for the comparison with the levels of this compound obtained from air-vegetation partition, as will be explained in detail below.

Modelled BaP concentrations in the atmosphere (Figure 3) achieve a maximum during the winter months (DJF), that can reach over 300 pg m^{-3} in most polluted areas (NW Spain and western coast of Portugal), while background areas hardly exceed 5 pg m^{-3} (lowest concentrations in the SE Levantine coast). The highest BaP concentrations ~~registered~~ measured using pine needles as the biomonitoring matrix and atmospheric concentrations simulated by the model were found in urban and industrial settings, mainly distributed along the north-western coast of the Iberian Peninsula (as also reported by Amigo et al., 2011 and Ratola et al., 2012) followed by rural and remote areas. This reflects the accumulation of anthropogenic sources like traffic, building heating or industrial processes involving combustions in the most populated areas of the Iberian Peninsula. Due to the characteristics of such sources, a tendency to seasonality can be anticipated as well. In the colder months, traffic and building heating are increased and this is not only reflected by the field measurements (Ratola et al., 2010), but also by the models, as shown in Figure 3.

Given that the model represents accurately the air climatologies of BaP, can we use its results to evaluate the ability of the air/vegetation methods available in scientific literature to estimate the atmospheric levels of BaP from biomonitoring databases? Being the accuracy of the model to capture the air concentrations evaluated against EMEP air measurements, the argument this work adopts is: since the model correctly captures air concentrations and deposition (which have been previously assessed in Section 3.1.1), we can use the modelled air concentrations as a reference to evaluate the fitness of the different vegetation-air conversion approaches. Therefore, i~~I~~n the following section, the model concentrations have been considered as a consistent reference (due to the low biases obtained) to act as a reference to validate the approaches for this vegetation-to-air conversion.

3.2 Comparison of vegetation-to-air approaches

Databases on the atmospheric levels of SVOCs are already available, but the existing ones (like EMEP) do not cover, for instance, the entire Iberian Peninsula for a climatologically-representative period of time (apart from some isolated measurements). In terms of vegetation, the scenario is even worse, but since the presence of SVOCs in such environmental matrices (and in particular in pine needles) reflects entirely an entrapment from the atmosphere (Hwang and Wade, 2008), these measured data can be used not only to validate the model results in vegetation but also to complement the information gathered by the direct atmospheric sampling. For that purpose, six approaches to convert the concentrations found in the 70 sites where pine needles were collected into atmospheric levels were compared to the reference provided by the CTM simulations. This hypothesis is based on the fact that models represent correctly the measured atmospheric concentrations of BaP over the Iberian Peninsula, taking into account the evaluation against EMEP field measurements available. This hypothesis was forced by the lack of simultaneous samplings of vegetation and air concentrations over the target area. Therefore, we used the following methodology: (a) validate simulations with WRF+CHIMERE data against EMEP network measurements, in order to check the ability of the CTM to reproduce atmospheric concentrations over the entire Iberian Peninsula; (b) once proven that errors are acceptable and that the model shows no trend bias, use modelled atmospheric concentrations as a consistent reference that allows us to compare various vegetation-to-air estimating methods and check which is the most suitable approach for the particular conditions of the area.

It is clear that given the numerous variables and conditions involved, the uptake processes of compounds like PAHs by matrices such as pine needles is not entirely understood (Barber et al., 2004). But the information we have so far indicates that pine needles are valid biomonitors of atmospheric loads, but also can be used to assess the performance of different methods to convert vegetation uptake levels into atmospheric concentrations. Thus, the objective is to test the response of the six vegetation-to-air approaches detailed in section 2.3 through a field/model check in the sampling points chosen.

Results (Table 2) reveal that approach 1d is the best fit to convert the levels measured in vegetation into air concentrations, when compared to the outcome provided by the model. This approach was used by Ratola and Jiménez-Guerrero (2015) to assess differences between pine species in modelling simulations as the deposition velocity is in this case defined for an entire forest canopy and not for a given species. This general characteristic is seemingly giving this approach an advantage in terms of the vegetation-to-air calculations. The MFB ranges from -19% for spring (MAM) to a slight overestimation during winter (DJF, +9%), being the biases under 3 pg m^{-3} for all seasons. These errors are relatively low bearing in mind the diversity of the sampling sites considered in this work. Previous works have demonstrated the seasonal variability of PAHs uptake by pine needles (Hwang and Wade, 2008; Ratola et al., 2010), with the highest levels occurring in winter and the lowest in summer. However, these differences are much more visible in the lighter PAHs (the ones in the gas-phase), given the stronger affinity of the pine needles waxy layer towards their entrapment, when compared to the particulate PAHs.

Being one of the latter, BaP in pine needles may not experience the same level of seasonal variation as in the atmosphere, even if it presents a similar trend. These seasonal differences can be much stronger in the atmosphere, due to the fluctuation of the emission rates from winter to summer. It is then not surprising that the model underestimates the atmospheric concentrations of BaP measured in the colder months and overestimates them in the warmer ones, since in this case the field values are obtained from the levels found in the pine needles. Approach 1d is also the best representation for this seasonal variability (estimated as the standard deviation between approaches and the CTM). Additionally, this approach shows the best air/vegetation relationship simulated by the model, with the rest of the methods providing unrealistic concentrations when compared to the measurements in EMEP stations and modelling results. In fact, approaches 1a and 2 tend to underestimate the modelled concentrations by a factor up to 10, yielding negative biases for all seasons. The rest of the approaches greatly overestimate the levels of BaP (by a factor of 100 in the case of 1c and 3 and of 1000 in approach 1b). These large variations are mainly caused by the difference in the deposition velocities used in each approaches 1a to 1d (from 10.8 m h^{-1} in 1a to 0.0039 m h^{-1} in 1b) and in completely different vegetation-to-air estimation strategies in approaches 2 and 3. The deposition velocity has an important role in one of the three methodologies for estimating air concentrations from vegetation (methodology which derives into approaches 1a to 1d), but it allows precisely to understand the differences that may occur when conditions are changed (different species, different locations, different times of the year in the same locations, different affecting sources, etc).

With respect to the temporal correlation coefficients, since approaches 1a to 1d present the same value (0.51), as they rely on the same calculations (only changing the deposition velocity). This is an acceptable description of the temporal variability observed in all sites. Approach 2 is not able to reproduce these time series (correlation coefficient of -0.55), but, interestingly, it is approach 3 that presents the best correlation (0.80). In this latter case, although the bias for the BaP concentrations is quite high, the *r* value can be related with the different uptake efficiencies pine needles show for gas-phase or particulate PAHs. The two equations suggested by Chun (2011) to relate concentrations of PAHs in needles and air separate the lighter from the heavier ones. So even if the actual concentrations are not very well described, the temporal air-needles synergies may better projected by this approach in this particular case.

Finally, spatial correlation coefficients (which provide a simulation for the adequate representation of the BaP spatial patterns over the Iberian Peninsula) are correctly reproduced by all approaches (Table 2). The highest value is seen for winter in approach 2 (r=0.68) and for the rest of the seasons, approaches 1a-1d present the higher correlation coefficients (from 0.67 in JJA to 0.85 in MAM). Approach 3 generally offers the lowest spatial correlation coefficients for all seasons, except in summer. The fact that the lowest *r* values are generally found for winter and summer (~~when~~ also the extremes of BaP concentrations ~~are found~~ in the environment), highlights the limitations of the model to represent these extremes.

Ideally, the air levels SVOCs are measured in the field using expensive active air sampling equipment which also require permanent power supply while operating. Thus, these devices only exist in certain parts of the world, which does not allow a proper coverage of the global presence of such contaminants, which naturally hinders the efforts of modelling estimation as well. As mentioned above, as living structures vegetation matrices have morphological, physical and chemical behaviour that depends on many parameters, even within the same species. Thus, the equations describing the air-vegetation partition suffer from these effects when a broad solution is searched for. Again in ideal terms, only a direct comparison of field campaigns and active air sampling performed in the same spots is bound to achieve some accuracy, if it includes a seasonal framework as well. In fact, the main approaches presented in this work derive from these type of combined studies. But when it is impossible to have simultaneous active air and biomonitoring sampling models can help us to assess if the assumptions we are working with are sound, if a previous validation with the field-based air concentrations is successful (as is the case in our study). Naturally, there is a concern that the uncertainty associated to all the steps involved may affect the conclusions of a study like this. Even if a detailed analysis would be extremely complex and out of the scope of this work, the main source of uncertainty of our global process can be identified: the emission inventories for PAHs, as stated by San José et al. (2013). In general, this uncertainty was estimated to be within a factor of 2 to 5 (Berdowski et al., 1997), much larger than any other uncertainty associated to the validation process and rest of steps. For instance, EMEP individual measurements should have a precision within ±10% and the data quality objectives for the sampling and chemical analysis set a combined uncertainty between 15 and 25% (EMEP, 2001). Also, the analytical methodology to quantify BaP in pine needles have similar precision values (Ratola et al., 2009). The contribution of these processes to the global uncertainties would be reduced in comparison to the BaP emissions.

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4 Conclusions

This work proved the good performance of pine needles as biomonitors of the BaP atmospheric concentrations. Results show that the WRF+CHIMERE modelling system reproduces accurately not only the atmospheric presence of BaP, with deviations below 0.4 ng g^{-1}, but also the spatial and temporal patterns of its concentrations over the vegetation in the Iberian Peninsula (biases lower than 30% for all stations and seasons). From the six methods tested to convert vegetation levels (in pine needles) into atmospheric concentrations, approach 1d showed the most accurate results, followed by approach 1a, when compared to modelling results and observations from EMEP. However, these results should not be interpreted as a ranking of the general performance of the approaches. For instance, given that approaches 1a, 1b, 1c and 1d only differ on the deposition velocity considered for BaP, we can conclude that approach 1d is the one representing more closely the particular conditions of the target area. Nevertheless, for other locations and frameworks, further research should be conducted to verify these conclusions. Another very important aspect to take into account is that none of the studies where the available approaches were reported used needles from the same pine species of the current study nor was located in areas of similar climatic or geographical conditions. These facts can considerably alter the uptake conditions of the pollutants, hence the different deposition rates reported.

Arguably, it could be said that when the model is taken as the reference, the deposition velocity in the best approach is not the most adequate for the Iberian Peninsula, but rather the one closer to the approximation of the deposition over vegetal canopies included in the CTM. This suggestion can be rebutted given that the model results were validated against the field data available from the EMEP air sampling stations, proving that the approximation of the model is indeed the most satisfactory for the conditions of this area (and, therefore, so are those of approach 1d). Another unprecedented perspective introduced by this work is that, contrary to the few similar studies found in literature, instead of studying isolated episodes of contamination, the simulations cover a large period (2006-2010). This ~~supposes~~ highlights a climatic viewpoint to the problem~~atic~~ of BaP on a regional scale, and was not done previously (at least over the Iberian Peninsula).

Considering that the theoretical principles of the three methodologies chosen in this work that led to the air-vegetation partition calculations are valid worldwide and having some of the parameters missing for our sampling domain, we had to resort to the ones existing in literature. With more similar studies in the future we can head towards a much better reproducibility and robustness of the modelling strategies. Our aim was to open a possible path for it and the results are encouraging. But if ~~field work~~fieldwork continues to be as scarce as it is nowadays, the journey will be necessarily slower than we hope for.

The relevance of these findings open the possibility that pine needles can be used to assess the temporal and spatial behaviour of BaP or other priority pollutants under completely innovating perspectives. Namely allowing a reliable understanding of the air quality in areas where common air sampling devices are unavailable. The comparison of levels within a regional scale will enable the strong enhancement of the knowledge available so far in the scientific literature for studies on atmospheric chemistry and transport of trans-boundary SVOCs, which is scarce (even more if we consider model validation against experimental data). Despite these promising results, further research is still needed and should be devoted to: (a) study the applicability of the methods tested to different areas (both geographically and in terms of land use) and (b) assess the performances of different vegetation species and their ability to act as biomonitors of the atmospheric presence of several classes of hazardous compounds.

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Supporting information available

Information on pine needles characteristics, sampling, analytical methodology, as well as on the modelling and vegetation-to-air estimation strategies. This material is available free of charge via the Internet.

References

Amigo, J. M., Ratola, N., and Alves, A.: Study of geographical trends of polycyclic aromatic hydrocarbons using pine needles, Atmos. Environ., 45, 5988-5996, 2011.

Augusto, S., Máguas, C., Matos, J., Pereira, M. J., and Branquinho, C.: Lichens as an integrating tool for monitoring PAH atmospheric deposition: A comparison with soil air and pine needles, Environ. Pollut., 158, 483–489, 2010.

Aulinger, A., Matthias, V., and Quante, M.: An approach to temporally disaggregate benzo(a)pyrene emissions and their application to a 3D Eulerian atmospheric chemistry transport model, Wat. Air Soil Pollut., 216, 643-655, 2011.

Baek, S. O., Field, R. A., Goldstone, M. E., Kirk, P. W., Lester, J. N., and Perry, R.: A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behaviour, Wat. Air Soil Pollut., 60, 279-300, 1991.

Barber, J. L., Thomas, G. O., Kerstiens, G., and Jones, K. C.: Current issues and uncertainties in the measurement and modelling of air–vegetation exchange and within-plant processing of POPs, Environ. Pollut., 128, 99-138, 2004.

Baussant, T., Sanni, S., Jonsson, G., Skadsheim, A., and Borseth, J. F.: Bioaccumulation of polycyclic aromatic compounds: 1. Bioconcentration in two marine species and in semipermeable membrane devices during chronic exposure to dispersed crude oil, Environ. Toxicol. Chem., 20, 1175-1184, 2001.

Berdowski, J. J. M., Baas, J., Bloos, J. P. J., Visschedijk, A. J. H. and Zandveld, P. Y. J.: The European Atmospheric Emission Inventory for Heavy Metals and Persistent Organic Pollutants, Umweltforschungsplan des Bundesministers fur Umwelt, Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungbericht 104 02 672/03. TNO, Apeldoorn, The Netherlands, 1997.

Bernalte, E., Marín-Sánchez, C., Pinilla-Gil, E., Cerceda-Balic, F., and Vidal-Cortex, V.: An exploratory study of particulate PAHs in low-polluted urban and rural areas of southwest Spain: concentrations, source assignment, seasonal variation and correlations with other pollutants, Wat. Air Soil Pollut., 223, 5143-5154, 2012.

Bidleman, T. F.: Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning, Environ. Sci. Technol., 22, 361–367, 1988.

Bieser, J., Aulinger, A., Matthias, V., and Quante, M.: Impact of emission reductions between 1980 and 2020 on atmospheric benzo[a]pyrene concentrations over Europe, Wat. Air Soil Pollut., 223, 1391-1414, 2012.

Cape, J. N., Paterson, I., and Wolfenden, S. J.: Regional variation in surface properties of Norway spruce and Scots pine needles in relation to forest decline, Environ. Pollut., 58, 325-342, 1989.

Chun, M. Y.: Relationship between PAHs concentrations in ambient air and deposited on pine needles, Environ. Health Toxicol., 26, 6 p, 2011.

Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union L 152, 1–44, 2008.

EMEP (European Monitoring and Evaluation Programme): EMEP manual for sampling and chemical analysis. EMEP/CCC-Report 1/1995 - revised. Norwegian Institute for Air Research, Kjeller, Norway, November 2001.

Friedman, C. L., and Selin, N. E.: Long-range atmospheric transport of polycyclic aromatic hydrocarbons: a global 3-D model analysis including evaluation of Arctic sources, Environ. Sci. Technol., 46, 9501–9510, 2012.

Galarneau, E., Makar, P. A., Zheng, Q., Narayan, J., Zhang, J., Moran, M. D., Bari, M. A., Pathela, S., Chen, A., and Chlumsky, R.: PAH concentrations simulated with the AURAMS-PAH chemical transport model over Canada and the USA, Atmos. Chem. Phys. Discuss., 13, 18417-18449, 2013.

Giorgi, F.: A particle dry deposition scheme for use in tracer transport models, J. Geophys. Res., 91, 9794–9806, 1986.

Horstmann, M., and McLachlan, M. S.: Atmospheric deposition of semivolatile organic compounds to two forest canopies, Atmos. Environ., 32, 1799-1809, 1998.

Hwang, H. H., and Wade, T. L.: Aerial distribution, temperature-dependent seasonal variation, and sources of polycyclic aromatic hydrocarbons in pine needles from the Houston metropolitan area, Texas, USA, J. Environ. Sci. Health A, 43, 1243-1251, 2008.

Jakeman, A. J., Letcher, R. A., and Norton, J. P.: Ten iterative steps in development and evaluation of environmental models, Environ. Model. Soft., 21, 602-614, 2006.

Jiménez-Guerrero, P., Jorba, O., Baldasano, J. M., and Gassó, S.: The use of a modelling system as a tool for air quality management: annual high-resolution simulations and evaluation, Sci. Total Environ., 390, 323-340, 2008.

Klánová, J., Čupr, P., Baráková, D., Šeda, Z., Anděl, P., and Holoubek, I.: Can pine needles indicate trends in the air pollution levels at remote sites? Environ. Pollut., 157, 3248-3254, 2009.

Lammel, G., Sehili, A. M., Bond, T. C., Feichter, J., and Grassl, H.: Gas/particle partitioning and global distribution of polycyclic aromatic hydrocarbons - a modelling approach, Chemosphere, 76, 98-106, 2009.

Lehndorff, E., and Schwark, L.: Biomonitoring airborne parent and alkylated three-ring PAHs in the Greater Cologne Conurbation II: Regional distribution patterns, Environ. Pollut., 157, 1706-1713, 2009.

Mackay, D.: Multimedia Environmental Models: the Fugacity Approach, Lewis Pub., Chelsea, MI, 1991.

Maddalena, R. L., McKone, T. E., and Riley, W. J.: Is there a “forest filter effect” for organic pollutants? Stoch. Environ. Res. Risk Assess., 17, 231-234, 2003.

Mastral, A. M., and Callén, M. S.: A review on polycyclic aromatic hydrocarbon (PAH) emission from energy generation, Environ. Sci. Technol., 34, 3051−3057, 2000.

Matthias, V., Aulinger, A., and Quarte, M.: CMAQ simulations of the benzo(a)pyrene distribution over Europe for 2000 and 2001, Atmos. Environ., 43, 4078-4086, 2009.

Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Blond, N., Colette, A., Coll, I., Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J. L., Pison, I., Siour, G., Turquety, S., Valari, M., Vautard, R., and Vivanco, M.G.: CHIMERE 2013: a model for regional atmospheric composition modelling, Geosci. Model Dev., 6, 981-1028, 2013.

Morville, S., Delhomme, O., and Millet, M.: Seasonal and diurnal variations of PAH concentrations between rural, suburban and urban areas, Atmos. Pollut. Res., 2, 366-373, 2011.

Odabasi, M., Cetin, E., and Sofuoglu, A.: Determination of octanol–air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas–particle partitioning in an urban atmosphere, Atmos. Environ., 40, 6615–6625, 2006.

Peters, K., and Eiden, R.: Modelling the dry deposition velocity of aerosol particles to a spruce forest, Atmos. Environ., 26, 2555–2564, 1992.

Piccardo, M. T., Pala, M., Bonaccurso, B., Stella, A., Redaelli, A., Paola, G., and Valério, F.: *Pinus nigra* and *Pinus pinaster* needles as passive samplers of polycyclic aromatic hydrocarbons, Environ. Pollut., 133, 293-301, 2005.

Pöschl, U.; Letzel, T.; Schauer, C.; Niessner, R., Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[a]pyrene: O_3 and H_2O adsportion, benzo[a]pyrene degradation, and atmospheric implications, J. Phys. Chem. A, 105, 4029-4041, 2001.

Ratola, N., Amigo, J. M., Oliveira, M. S. N., Araújo, R., Silva, J. A., and Alves, A.: Differences between *Pinus pinea* and *Pinus pinaster* as bioindicators of polycyclic aromatic hydrocarbons, Environ. Exp. Bot., 72, 339-347, 2011.

Ratola, N., and Jiménez-Guerrero, P.: Combined field/modelling approaches to represent the air-vegetation distribution of benzo[a]pyrene using different vegetation species, Atmos. Environ., 106, 34-42, 2015.

Ratola, N., Alves, A., Lacorte, S., and Barceló, D.: Distribution and sources of PAHs using three pine species along the Ebro river, Environ. Monit. Assess., 184, 985-999, 2012.

Ratola, N., Amigo, J. M., and Alves, A.: Comprehensive assessment of pine needles as bioindicators of PAHs using multivariate analysis. The importance of temporal trends, Chemosphere, 81, 1517-1525, 2010.

Ratola, N., Amigo, J. M., and Alves, A.: Levels and sources of PAHs in selected sites from Portugal: biomonitoring with *Pinus pinea* and *Pinus pinaster* needles, Arch. Environ. Con. Toxicol., 58, 631-647, 2010.

Ratola, N., Lacorte, S., Barceló, D., and Alves, A.: Microwave-assisted extraction and ultrasonic extraction to determine polycyclic aromatic hydrocarbons in needles and bark of *Pinus pinaster* Ait. and *Pinus pinea* L. by GC-MS, Talanta, 77, 1120-1128, 2009.

San José, R., Pérez, J. L., Callén, M. S., López, J. M., and Mastral, A.: BaP (PAH) air quality modelling exercise over Zaragoza (Spain) using an adapted version of WRF-CMAQ model, Environ. Pollut., 183, 151-158, 2013.

Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M.: Environmental Organic Chemistry. 2nd ed.; John Wiley & Sons, Hoboken, New Jersey, 2003.

Sehili, A. M., and Lammel, G.: Global fate and distribution of polycyclic aromatic hydrocarbons emitted from Europe and Russia, Atmos. Environ., 41, 8301-8315, 2007.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: from Air Pollution to Climate Change. Wiley- Interscience, New Jersey, 1997.

Simonich, S., and Hites, R.: Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons, Environ. Sci. Technol., 28, 939-943, 1994.

Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O., Barker, D. M., and Duda, M. G.: A description of the Advanced Research WRF Version 3. NCAR technical note NCAR/TN20201c475+STR, http://www.mmm.ucar.edu/wrf/users/docs/arw v3.pdf, 2008.

Solé, M.: Assessment of the results of chemical analyses combined with the biological effects of organic pollution on mussels, Trends Anal Chem., 19, 1–8, 2000.

St-Amand, A. D., Mayer, P. M., and Blais, J. M.: Modeling atmospheric vegetation uptake of PBDEs using field measurements, Environ. Sci. Technol., 41, 4234-4239, 2007.

St-Amand, A. D., Mayer, P. M., and Blais, J. M.: Modeling PAH uptake by vegetation from the air using field measurements, Atmos. Environ., 43, 4283-4288, 2009a.

St-Amand, A. D., Mayer, P. M., and Blais, J. M.: Prediction of SVOC vegetation and atmospheric concentrations using calculated deposition velocities, Environ. Int., 35, 851-855, 2009b.

Tomashuk, T. A.: A comparison of atmospheric PAHs in pine needles and high-volume sampler filters in the Dayton metro area. MSc Thesis, Wright State University, Dayton OH, 83 pp., 2010.

Torseth, K., Aas, W., Breivik, K., Fjaeraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009, Atmos. Chem. Phys., 12, 5447–5481, 2012.

Tremolada, P., Burnett, V., Calamari, D., and Jones, K. C.: Spatial distribution of PAHs in the UK atmosphere using pine needles, Environ. Sci. Technol., 30, 3570-3577, 1996.

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and Tarrasón, L.: Evolution of NOx emissions in Europe with focus on road transport control measures, Atmos. Chem. Phys., 9, 1503-1520, 2009.

Weiss, P., Lorbeer, G., and Scharf, S.: Regional aspects and statistical characterisation of the load with semivolatile organic compounds at remote Austrian forest sites, Chemosphere, 40, 1159-1171, 2000.

Wesely, M.: Parameterization of surface resistances to gaseous dry deposition in regional scale numerical models, Atmos. Environ., 23, 1293–1304, 1989.

Zhang, L., Gong, S., Padro, J., and Barrie, L.: A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmos. Environ., 35, 549–560, 2001.

TABLE AND FIGURE CAPTIONS

Table 1. Seasonal evaluation of WRF+CHIMERE modelled BaP depositions results (over vegetal canopies) against concentrations found in pine needles.

Table 2. Results from the comparison of BaP concentrations in air obtained by the chemistry transport models (CTM) simulations and those estimated from pine needle levels by several approaches

Figure 1. Seasonal distribution of modelled deposition of BaP on vegetation (ng g^{-1}) over the domain covering the Iberian Peninsula: (from top-down and left-right): winter (DJF), spring (MAM), summer (JJA) and autumn (SON) climatologies for the period 2006-2010.

Figure 2. BaP annual mean concentrations (pg m^{-3}, shaded) and biases for EMEP stations (pg m^{-3}, circles) using the available information for the period 2006-2010.

Figure 3. BaP climatologies (pg m^{-3}) over the Iberian Peninsula (from top-down and left-right): winter (DJF), spring (MAM), summer (JJA) and autumn (SON) for the period 2006-2010.

Table 1. Seasonal evaluation of WRF+CHIMERE modelled BaP depositions results (over vegetal canopies) against measured concentrations found in pine needles.

	DJF	**MAM**	**JJA**	**SON**
MFB (%)	-2.17	16.77	-39.23	5.28
RMSE (ng g^{-1})	1.26	1.45	0.84	1.97
BIAS (ng g^{-1})	0.10	0.08	-0.41	0.17
OBS MEAN±STD DEV (ng g^{-1})	1.67±1.66	2.39±2.17	1.25±0.90	1.85±1.64
MOD MEAN (ng g^{-1})	1.76±1.70	2.48±2.37	0.84±0.64	2.02±1.42
SPATIAL CORR~~.~~ COEF~~.~~ (*r*)	0.86	0.87	0.85	0.77

DJF – December, January and February; MAM – March, April and May; JJA – June, July and August; SON – September, October and November; MFB - mean fractional bias; RMSE - root mean square error; OBS - pine needle concentrations; STD DEV – standard deviation; MOD - modelled concentrations; CORR~~.~~ COEF~~.~~ – correlation coefficient

Table 2. Results from the comparison of BaP concentrations in air obtained by the chemistry transport models (CTM) simulations and those estimated from levels measured in pine needles ~~levels~~ by several approaches

	DJF	MAM	JJA	SON
CTM MEAN*±STD DEV (pg m^{-3})	15.63±15.55	16.08±15.48	7.32±6.84	11.19±10.35
APPROACH 1a (TEMPORAL CORR. COEF.: 0.51)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF.	0.57	0.85	0.67	0.80
MFB (%)	-125.46	-129.35	-125.75	-136.06
RMSE (pg m^{-3})	19.09	16.14	8.11	14.57
BIAS (pg m^{-3})	-12.70	-12.58	-6.01	-9.64
METHOD MEAN±STD DEV (pg m^{-3})	3.31±3.24	3.51±3.21	1.31±1.01	1.55±1.21
APPROACH 1b (TEMPORAL CORR~~.~~ COEF~~.~~: 0.51)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF. (r)	0.57	0.85	0.67	0.80
MFB (%)	198.97	198.81	198.83	198.95
RMSE (pg m^{-3})	12526.82	16294.77	4413.82	5197.87
BIAS (pg m^{-3})	9203.00	9945.01	3815.12	4481.39
METHOD MEAN±STD DEV (pg m^{-3})	9219±8358~~.53~~	9961~~.09~~±9722~~.54~~	3822~~.44~~±2890~~.48~~	4492~~.58~~±3424~~.55~~
APPROACH 1c (TEMPORAL CORR~~.~~ COEF~~.~~: 0.51)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF. (r)	0.57	0.85	0.67	0.80
MFB (%)	193.27	192.28	193.06	193.15
RMSE (pg m^{-3})	1860.48	2420.65	653.60	765.74
BIAS (pg m^{-3})	1361.62	1474.44	563.88	660.15
METHOD MEAN±STD DEV (pg m^{-3})	1377.63±1347.92	1488.53±1400.05	571.20±431.94	671.34±511.74
APPROACH 1d (TEMPORAL CORR~~.~~ COEF~~.~~: 0.51)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF. (r)	0.57	0.85	0.67	0.80
MFB (%)	9.21	-18.99	-6.30	-15.58
RMSE (pg m^{-3})	18.34	12.42	5.91	9.45
BIAS (pg m^{-3})	0.08	-0.81	-0.84	-2.88
METHOD MEAN±STD DEV (pg m^{-3})	15.94±15.60	15.27±14.86	6.48±4.96	8.31±8.19
APPROACH 2 (TEMPORAL CORR~~.~~ COEF~~.~~: -0.55)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF. (r)	0.68	0.89	0.35	0.76
MFB (%)	-179.73	-171.63	-115.84	-121.53
RMSE (pg m^{-3})	21.01	19.09	8.22	13.70
BIAS (pg m^{-3})	-15.33	-14.96	-5.81	-8.89
METHOD MEAN±STD DEV (pg m^{-3})	0.68±0.60	1.13±1.06	1.51±1.15	2.30±2.24
APPROACH 3 (TEMPORAL CORR~~.~~ COEF~~.~~: 0.80)				
	DJF	**MAM**	**JJA**	**SON**
SPATIAL CORR. COEF. (r)	0.26	0.48	0.65	0.41
MFB (%)	194.93	194.88	197.07	195.66
RMSE (pg m^{-3})	1212.05	1166.83	897.97	916.64
BIAS (pg m^{-3})	1283.79	1214.75	967.09	986.96
METHOD MEAN±STD DEV (pg m^{-3})	1299.80±342.94	1230.83±333.38	974.41±36.72	998.15±41.59

*Modelling results are considered as a consistent reference to compare the estimations from the different approaches. DJF – December, January and February; MAM – March, April and May; JJA – June, July and August; SON – September, October and November; CTM – chemistry transport model concentrations; STD DEV – standard deviation; CORR~~.~~ COEF~~.~~ – correlation coefficient; MFB - mean fractional bias; RMSE - root mean square error

Supporting Information

Can biomonitors effectively detect airborne benzo[a]pyrene? An evaluation approach using modelling~~Can we use modelling methodologies to assess airborne benzo[*a*]pyrene from biomonitors? A comprehensive evaluation approach~~

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Pine needles analysis and quantification

Duplicate samples of 5 g of needles underwent ultrasonic extraction (USE) with a mixture of hexane:dichloromethane (1:1) as solvent and were subsequently cleaned-up using 5g alumina solid-phase extraction (SPE) cartridges from International Sorbent Technology (Mid Glamorgan, UK), using the same solvent for elution. After blowing down to dryness and solvent change to hexane, chromatographic analysis of BaP was done in a Varian CP-3800 gas chromatograph (Lake Forest, CA, USA) coupled to a Varian 4000 mass spectrometer in Portugal and a Trace GC 2000 Series gas chromatograph from TermoQuest (Waltham, MA, USA) coupled to a Finnigan Trace MS 2000 Series mass spectrometer in Spain. However, the operation was similar in both cases, namely using electron impact ionization (70 eV), a J&W Scientific (Folsom, CA, USA) 30 m × 0.25 mm I.D. DB-5 column coated with 5% diphenylpolydimethylsiloxane (film thickness 0.25 μm) and the same oven temperature program. The injector, transfer line and ion source temperatures were also the same (280, 250 and 200 ºC, respectively). Finally, the acquisition was made in single ion monitoring (SIM) mode using deuterated PAHs as surrogate standards. BaP was identified and quantified using retention time and up to three ions, with perylene-d_{12} acting as surrogate standard and anthracene-d_{10} as internal standard to look for GC-MS errors.

Linear behaviour between 0.01 and 1 mg L^{-1} and good chromatographic resolution was obtained for BaP, with a limit of detection below 0.10 ng g^{-1} (dry weight). The BaP concentrations were calculated in dry weight, after determining the water content of the needles for each species (Table S1). This information is needed for the estimates of air concentrations from the levels found in pine needles, as detailed below.

Table S1. Characteristics of the four pine needle species employed in this study.

	P. pinea	***P. pinaster***	***P. halepensis***	***P. nigra***
Mean mass of one needle (g)[a]	0.06	0.13	0.018	0.035
Mean surface area (m^2x10^{-6})[a]	545	815	254	366
Lipid content (mg g^{-1}, dw)	121.95	182.93	105.56	104.26
Water content (% mass)	59	59	46	53

[a] Data taken from Daligault (1991) and Moro (2006)

Modelling experiment

Table S2. Set of parameterisations used in the WRF+CHIMERE modelling system

WRF	**CHIMERE**
Microphysics → **WSM3**	Chemical Mechanisms → **MELCHIOR2**
PBL → **Yonsei University**	Aerosol chemistry → Inorganic (thermodynamic equilibrium with **ISORROPIA**) and organic (**MEGAN SOA** scheme) aerosol chemistry
Radiation → **CAM**	Natural aerosols → **dust**, **re-suspension and inert sea-salt**
Soil → **Noah LSM**	BC → **LMDz-INCA+GOCART**
Cumulus → **Kain-Fritsch**	

The Advanced Research Weather Research and Forecasting (WRF-ARW) Model v3.1.1 (Klemp et al., 2007; Skamarock et al., 2008) is used to provide the meteorology to the chemistry transport models. WRF is a fully compressible, Eulerian non-hydrostatic model that solves the equations that govern the atmospheric motions. 33 vertical layers on sigma coordinates cover from the ground level up to 10 hPa. Microphysical processes are treated using the single-moment 3-class scheme described in Hong et al. (2004). The sub-grid-scale effects of convective and shallow clouds are resolved by a modified version of the Kain-Fritsch scheme based on Kain and Fritsch (1993). The Noah land surface model was used to solve the soil processes on 4 layers to a depth of 2m (Chen and Dudhia, 2001a; 2001b). The vertical sub-grid-scale fluxes caused by eddy transport in the atmospheric column are resolved by the Yonsei University non-local planetary boundary layer scheme (Noh et al., 2003). Finally, radiation was treated through the Community Atmospheric Model (CAM) 3.0 radiation scheme (Collins et al., 2006).

WRF was coupled off-line to CHIMERE. Atmospheric concentrations of BaP have been calculated using CHIMERE chemistry transport model (v2008b), coupled off-line to WRF outputs and EMEP emissions. ~~This CHIMERE version includes gaseous and particulate BaP and its degradation by OH radicals, which represents over 99% of the degradation path for BaP (Bieser et al., 2012).~~ For further details on the model options, the reader is referred to Menut et al. (2013). MELCHIOR2 gas-phase mechanism is implemented within CHIMERE.

The chemistry transport model includes aerosol and heterogeneous chemistry; distinguishes among different chemical aerosol components, namely nitrate, sulphate, ammonium, elemental and organic carbon with three subcomponents (primary, secondary anthropogenic and secondary biogenic) and marine aerosols. Unspecified primary anthropogenic aerosols and aerosol water are additionally kept as separate components. The model considers the thermodynamic equilibrium using the ISORROPIA model (Nenes et al., 1998). Last, the aerosol microphysical description for CHIMERE is based on a sectional aerosol module including 6 bins from 10 nm to 40 µm using a geometrical progression. Moreover, a dynamical approach is used to describe the gas/particle conversion, in line with Bowman et al. (1997):

$$Ji = 1/ \tau i (Gi - Gi_{eq})$$

Where Ji (µg m^{-3} s^{-1}) is the absorption or desorption flux of species i; τi (s) is a characteristic time of the mass transfer that is a function of particle size and the chemical properties of i; Gi is the bulk gas-phase concentration of i and Gi_{eq} is the gas-phase concentration of i at equilibrium. The gas-phase concentrations at equilibrium depend on the chemical composition of the particles, the temperature and, for hydrophilic species, the relative humidity (Pun et al., 2006).

In the present work, simulations covered the period 2006-2010. Initial and boundary conditions for WRF were provided by ERA-Interim reanalysis (Dee et al., 2011), while for CHIMERE, the global climate chemistry model LMDz-INCA2 was used (96 x 72 grid cells, namely 3.75° x 2.5° in longitude and latitude, with 19 sigma-p hybrid vertical levels, Szopa et al. (2009) developed by the Laboratoire des Sciences du Climat et l'Environnement (LSCE). Climatic monthly mean data are interpolated in the horizontal and vertical dimensions to force the major chemical concentrations at the boundaries of the domain. A detailed description of the INteractive Chemistry and Aerosol (INCA) model is presented by Hauglustaine et al. (2004) and Folberth et al. (2006). Because the contribution of long-range transport on ground level concentrations (those considered in this work) can be considered as negligible, the influence of using climatological boundary conditions is limited and overwhelmed by local processes.

Anthropogenic emissions for the entire period of simulations are derived from the EMEP database (Vestreng et al., 2009) and disaggregated to the working resolution following spatial proxy data, according to the methodology stated in Pay et al. (2010). For BaP emissions, data have been obtained from the EMEP-MSCEAST web site (http://www.msceast.org). The accuracy of simulations depends strongly on emission data and unfortunately there are strong uncertainties in BaP emissions, by a factor of 2 to 5 (San José et al., 2013). According to these authors, the main source of BaP is incomplete combustion processes of organic material, in particular wood and coal in private households. Industrial heating and cookeries as well as road traffic are also large sources of BaP, which is emitted in particle phase.

Natural emissions (of sea salt and dust) depend on meteorological conditions, and consequently they are coupled hourly to WRF meteorological outputs. Biogenic emissions were generated dynamically using MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006) with the parameterized form of the canopy environment model. The model estimates hourly isoprene, monoterpene, and other BVOC emissions based on plant functional type and as a function of hourly temperature and ground level shortwave radiation from WRF.

Model validation

EMEP stations are located at a minimum distance of approximately 10 km from large emission sources and thus assumed to fit the resolution of the model used for regional background concentrations (Torseth et al., 2012). Thus, as reported by Ratola and Jiménez-Guerrero (2015), results from the EMEP monitoring data were used to characterize the ability of the model to reproduce present air BaP levels and variability. The “EMEP Manual for Sampling and Analysis” (EMEP, 2001) describes all the sampling methodologies employed for each chemical and/or matrix and the recommended operation, as well as the data quality objectives for the yielded results. ~~Regarding the uncertainty, no information is given for the Iberian sites, but it should meet the EMEP data quality objectives for the combined sampling and chemical analysis (between 15 and 25%). This fulfillment (among others) leads to the validity of the results presented.~~ Final The available stations running in the Iberian Peninsula in the 2006-2010 time frame were: Niembro (2006-2010), Campisabalos (2007-2008), O Saviñao (2007), Víznar (2008-2010), Peñausende (2008-2009), Barcarrota (2008), Zarra (2008), San Pablo de los Montes (2009-2010), Mahón (2010) and Els Torms (2010). In all of them, BaP ~~measurements are available as weekly or monthly averages~~frequencies of measurement and duration varied probably depending on the budget limitations, but when sampling campaigns were active, they were performed usually once a week.~~.~~ ~~The results (available as weekly or monthly averages) have been~~were ~~compared to the available periods for observations.~~ The handling of samples is taken with extreme care to limit external contaminations and/or degradation reactions to occur. For the more volatile chemicals, there is a bigger risk of having some losses, but in the case of BaP, since it is almost all formed by particulate matter, it is bound to stay stable under the appropriate storage conditions (commonly in the freezer until analysis). The results (available as weekly or monthly averages) were compared to the available periods for observations. Regarding the uncertainty, no information is given for the Iberian sites, but it generally should meet the EMEP data quality objectives for the combined sampling and chemical analysis (between 15 and 25%) (EMEP, 2001).

Being well aware of the need for further measurements with a higher temporal coverage, the strong limitation (not only over the Iberian Peninsula, but worldwide) for simultaneous air and vegetation measurements forced us to rely on the best information available. In doing so, this work intends to set a starting point for an improvement in the design of sampling campaigns and associated modelling strategies. Although it was possible to find some data from air monitoring stations from the Generalitat de Catalunya and the Comunitat Valenciana, not all of them presented climatologically representative series. Thus, also to maintain a wider geographical coverage with under the same sampling and analytical framework to ensure the homogeneity of the data.

For the evaluation of canopy deposition and atmospheric concentrations, a number of statistical parameters have been selected (Figure S1). Spatial correlation coefficient (*r*), root mean square error (RMSE) and mean bias (MB) values are commonly used by the modelling community and have therefore been selected according to the criteria of Pay et al. (2010), who use them to evaluate a modelling system for Europe (~~.—~~“bias” is intended as the difference between modelled and observed means). Moreover, Boylan and Russell (2006) suggest that the mean normalised bias error (MNBE) for each model-observed pair by the observation is a useful parameter, but may not be appropriate for evaluating particulate matter and their components. These authors suggested the mean fractional bias (MFB) and the mean fractional error (MFE) instead, indicating that model performance goal would be met when both the MFE and MFB are less than or equal to 50% and ±30%, respectively, and the model performance criterion when MFE $\leq$ 75% and MFB $\leq$ ±60%. These criteria and goals have been selected to provide the metrics for the WRF+EMEP+CHIMERE evaluation of BaP. Annual and seasonal mean statistics are computed, with seasons corresponding to December, January and February (DJF, winter), March, April and May (MAM, spring), June, July and August (JJA, summer) and September, October and November (SON, autumn).

MOD MEAN (modelled concentrations)	$\frac{1}{N}\sum C_{mod}$
OBS MEAN (pine needle concentrations)	$\frac{1}{N}\sum C_{obs}$
BIAS	$\frac{1}{N}\sum (C_{mod} - C_{obs})$
RMSE (root mean square error)	$\sqrt{\sum \frac{(C_{mod}-C_{obs})^2}{N}}$
MFB (mean fractional bias)	$\frac{1}{N}\sum \left(\frac{(C_{mod}-C_{obs})}{\left(\frac{C_{mod}+C_{obs}}{2}\right)} \right)$

Figure S1. Main statistical parameters used in model validation

As our aim is to have the best approximation of atmospheric BaP levels through modelling procedures, to serve as a reference pseudo-reality to estimate the most accurate vegetation-to-air conversion method, the multiplicative ratio bias-~~correction~~ adjustment technique has been applied following the methodology of Borrego et al. (2011). The ~~correction~~ adjustment factor is calculated as the quotient between the additions of observed and modelled concentrations at a particular hour of the *n* previous days. Borrego et al. (2011) and Monteiro et al. (2013) recommend a four-day training period (n=4). However, given the limited availability of EMEP data (only on a weekly basis), a four-week training period has been chosen here instead as a compromise between having a sufficiently long timeframe to gather adequate statistics but not as much as to mask seasonal variations. This bias-adjustment technique improves the relative mean bias (expressed as percentage) by approximately 90% (Monteiro et al., 2013). However, the goal is to remove potential systematic model errors intrinsic to each model formulation or input data, rather than obtaining an additional assessment of the possible model flaws or performance or to correct them artificially. Figure S2 depicts the mathematical representation of this approach, with $C^{corrected}$, C^{model}, and C^{obs} as the bias-adjusted, original modelled and measured concentrations at a given hour “h” and day “day”.

$$C^{\mathrm{corrected}}(\mathrm{h}, \mathrm{day}) = -\frac{1}{n_{\mathrm{days}}} \sum_{n_{\mathrm{days}}} \left(C_{\mathrm{h}}^{\mathrm{model}} - C_{\mathrm{h}}^{\mathrm{obs}}\right) + C^{\mathrm{model}}(\mathrm{h}, \mathrm{day})$$

Figure S2. Mathematical expression for the bias-adjustment of the modelled results.

As stated in Monteiro et al. (2013), the global mean bias is minimised the for all the monitoring stations, using the bias detected in previous days for a given hour (h) of the day. These procedures are model, site, and time of day specific.

Results

Table S3. Parameters of the modelled deposition over vegetal canopies evaluated against observations compiled from pine needles, for all the sampling points (n – number of duplicate samples; mean concentrations in ng g^{-1}).

SITE	n	LAT~~ITUDE~~	LONG~~ITUDE~~	PINE SPECIES	BIAS	MFB	OBS. MEAN	MOD. MEAN
Alcolea de Cinca	1	42.03	-1.56	*Pinus pinea*	**-0.63**	**-95.41%**	**0.98**	**0.35**
Alcoutim	4	37.47	-7.47	*Pinus pinea*	**0.11**	**26.63%**	**0.81**	**0.92**
Antuã 1	4	40.69	-8.52	*Pinus pinea*	**-0.17**	**24.18%**	**2.71**	**2.53**
Barcelona	1	41.39	2.11	*Pinus pinea*	**-2.53**	**-105.46%**	**3.66**	**1.13**
Beja	4	38.01	-7.87	*Pinus pinea*	**-0.29**	**20.86%**	**1.02**	**0.73**
Braga	4	41.56	-8.40	*Pinus pinea*	**0.71**	**31.72%**	**0.96**	**1.67**
Castelo Branco	4	39.83	-7.50	*Pinus pinea*	**0.60**	**31.72%**	**0.81**	**1.41**
Coimbra	4	40.21	-8.42	*Pinus pinea*	**0.54**	**32.59%**	**0.62**	**1.16**
El Bocal	1	41.57	-0.69	*Pinus pinea*	**-0.49**	**-33.85%**	**1.71**	**1.21**
El Prat	1	41.30	2.10	*Pinus pinea*	**-0.38**	**-16.77%**	**2.44**	**2.06**
Évora	4	38.58	-7.91	*Pinus pinea*	**-1.13**	**6.74%**	**1.33**	**0.21**
Faro	4	37.02	-7.94	*Pinus pinea*	**-1.53**	**7.34%**	**1.85**	**0.32**
Leiria	4	39.75	-8.80	*Pinus pinea*	**0.34**	**29.56%**	**0.76**	**1.10**
Lisboa	4	38.72	-9.14	*Pinus pinea*	**-4.73**	**5.32%**	**5.37**	**0.64**
Loulé	4	37.13	-8.10	*Pinus pinea*	**-1.90**	**10.17%**	**2.56**	**0.65**
Maleján	1	41.82	-1.55	*Pinus pinea*	**-0.77**	**-91.95%**	**1.22**	**0.45**
Miranda de Ebro 1	1	42.68	-2.95	*Pinus pinea*	**-0.25**	**-70.21%**	**0.49**	**0.23**
Monteagudo	1	41.96	-1.69	*Pinus pinea*	**-0.34**	**-26.47%**	**1.46**	**1.12**
Movera	1	41.64	-0.80	*Pinus pinea*	**-0.01**	**-0.61%**	**1.22**	**1.21**
Outão	4	38.49	-8.98	*Pinus pinea*	**2.11**	**35.21%**	**1.53**	**3.64**
Portalegre	4	39.30	-7.43	*Pinus pinea*	**-0.01**	**24.89%**	**1.24**	**1.23**
Porto 1	4	41.18	-8.60	*Pinus pinea*	**1.08**	**31.13%**	**1.66**	**2.74**
Praia Verde	4	37.18	-7.48	*Pinus pinea*	**-0.22**	**17.50%**	**0.47**	**0.25**
Quintãs 1	4	40.58	-8.63	*Pinus pinea*	**0.80**	**33.80%**	**0.74**	**1.53**
Santarém	4	39.24	-8.69	*Pinus pinea*	**-0.73**	**16.55%**	**1.44**	**0.71**
Sines	4	37.96	-8.81	*Pinus pinea*	**0.03**	**25.51%**	**0.75**	**0.78**
Souselas	4	40.29	-8.41	*Pinus pinea*	**1.58**	**29.94%**	**3.20**	**4.78**
Torres de Segre	1	41.54	0.51	*Pinus pinea*	**-0.11**	**-7.74%**	**1.46**	**1.35**
Vic	1	41.94	2.25	*Pinus pinea*	**-0.71**	**-21.37%**	**3.66**	**2.95**
Villodas	1	42.83	-2.78	*Pinus pinea*	**1.91**	**98.82%**	**0.98**	**2.88**
Antuã 2	4	40.69	-8.52	*Pinus pinaster*	**-0.67**	**22.50%**	**3.71**	**3.03**
Bragança	4	41.81	-6.76	*Pinus pinaster*	**0.23**	**26.96%**	**1.37**	**1.60**
Caminha	4	41.87	-8.86	*Pinus pinaster*	**0.54**	**29.23%**	**1.33**	**1.87**
Estarreja	4	40.77	-8.57	*Pinus pinaster*	**1.34**	**31.68%**	**1.83**	**3.17**
Fóia	4	37.31	-8.61	*Pinus pinaster*	**0.84**	**35.29%**	**0.60**	**1.44**
Guarda	4	40.54	-7.27	*Pinus pinaster*	**0.66**	**29.41%**	**1.55**	**2.21**
Leça	4	41.22	-8.71	*Pinus pinaster*	**-0.63**	**23.80%**	**6.85**	**6.22**
Mirandela	4	41.37	-7.14	*Pinus pinaster*	**-1.14**	**18.88%**	**2.89**	**1.76**
Porto 2	1	41.18	-8.60	*Pinus pinaster*	**1.20**	**28.27%**	**3.66**	**4.86**
Quintãs 2	4	40.58	-8.63	*Pinus pinaster*	**-0.14**	**24.13%**	**2.07**	**1.93**
Rio de Onor	4	41.94	-6.61	*Pinus pinaster*	**0.73**	**31.06%**	**1.14**	**1.87**
Torre	4	40.31	-7.58	*Pinus pinaster*	**0.32**	**29.64%**	**0.71**	**1.03**
Vide	1	40.29	-7.78	*Pinus pinaster*	**1.19**	**65.60%**	**1.22**	**2.41**
Vila Real	4	41.30	-7.74	*Pinus pinaster*	**2.17**	**32.42%**	**2.57**	**4.74**
Arazuri	1	42.81	-1.72	*Pinus nigra*	**0.14**	**20.40%**	**0.64**	**0.78**
Briñas	1	42.59	-2.84	*Pinus nigra*	**1.30**	**75.67%**	**1.06**	**2.36**
La Bordeta	1	41.60	0.62	*Pinus nigra*	**-0.32**	**-117.75%**	**0.43**	**0.11**
Miranda de Ebro 2	1	42.67	-2.09	*Pinus nigra*	**-0.10**	**-27.59%**	**0.43**	**0.32**
Nestares	1	43.00	-4.15	*Pinus nigra*	**0.00**	**-0.10%**	**0.43**	**0.43**
Urdiáin	1	42.90	-2.14	*Pinus nigra*	**0.61**	**83.80%**	**0.43**	**1.04**
Amposta	1	40.72	0.58	*Pinus halepensis*	**-0.60**	**-39.43%**	**1.83**	**1.23**
Andosilla	1	42.37	-1.94	*Pinus halepensis*	**0.38**	**29.17%**	**1.10**	**1.48**
Caldearenas	1	42.40	-0.50	*Pinus halepensis*	**0.01**	**3.14%**	**0.37**	**0.38**
Cascante	1	41.98	-1.68	*Pinus halepensis*	**-0.44**	**-63.19%**	**0.92**	**0.48**
Cuarte de Huerva	1	41.61	-0.92	*Pinus halepensis*	**-0.33**	**-21.98%**	**1.65**	**1.32**

Table S3. (cont.) Parameters of the modelled deposition over vegetal canopies evaluated against observations compiled from pine needles, for all the sampling points (n – number of duplicate samples; mean concentrations in ng g^{-1}).

SITE	n	LAT~~ITUDE~~	LONG~~ITUDE~~	PINE SPECIES	BIAS	MFB	OBS. MEAN	MOD. MEAN
Deltebre	1	40.71	0.71	*Pinus halepensis*	-0.58	-37.70%	1.83	1.25
Estella/Lizarra	1	42.67	-2.03	*Pinus halepensis*	1.40	97.49%	0.73	2.13
Flix	1	41.23	0.55	*Pinus halepensis*	0.07	11.87%	0.55	0.62
Grisén	1	41.73	-1.18	*Pinus halepensis*	-1.22	-39.69%	3.67	2.45
Logroño 1	1	42.47	-2.44	*Pinus halepensis*	-0.44	-35.19%	1.47	1.03
Logroño 2	1	42.67	-2.42	*Pinus halepensis*	1.60	34.34%	3.85	5.45
Mollerussa	1	41.62	0.91	*Pinus halepensis*	-0.72	-77.74%	1.28	0.57
Puente La Reina	1	42.67	-1.82	*Pinus halepensis*	0.79	60.19%	0.92	1.71
San Adrián	1	42.33	-1.93	*Pinus halepensis*	-0.11	-8.91%	1.28	1.17
Sástago	1	41.32	-0.34	*Pinus halepensis*	-0.39	-72.55%	0.73	0.34
Tornabous	1	41.69	1.05	*Pinus halepensis*	-0.41	-77.45%	0.73	0.32
Tortosa	1	40.80	0.51	*Pinus halepensis*	-0.30	-16.01%	2.02	1.72
Tudela 1	1	42.07	-1.60	*Pinus halepensis*	-0.89	-35.90%	2.94	2.04
Tudela 2	1	42.08	-1.62	*Pinus halepensis*	-0.41	-25.29%	1.83	1.42
Villanueva de Gállego	1	41.77	-0.82	*Pinus halepensis*	-0.74	-31.16%	2.75	2.01

References

~~Bieser, J., Aulinger, A., Matthias, V., and Quante, M.: Impact of emission reductions between 1980 and 2020 on atmospheric benzo[a]pyrene concentrations over Europe, Wat. Air Soil Pollut., 223, 1391-1414, 2012.~~

Borrego, C., Monteiro, A., Pay, M. T., Ribeiro, I., Miranda, A. I., Basart, S., and Baldasano, J. M.: How bias-correction can improve air quality forecasts over Portugal., Atmos. Environ., 45, 6629-6641, 2011.

Bowman, F. M., Odum, J. R., Seinfeld, J. H., and Pandis, S. N.: Mathematical model for gas-particle partitioning of secondary organic aerosols. Atmos. Environ., 31, 3921-3931, 1997.

Boylan, J. W., and Russell, A. G.: PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models, Atmos. Environ., 40, 4946–495, 2006.

Chen, F., and Dudhia, J.: Coupling an advanced land surface hydrology model with the Penn State-NCAR MM5 modeling system. Part I: Model implementation and sensitivity, Mon. Weather Rev., 129, 569-585, 2001a.

Chen, F., and Dudhia, J.: Coupling an advanced land surface hydrology model with the Penn State-NCAR MM5 modeling system. Part II: Preliminary model validation, Mon. Weather Rev., 129, 587-604, 2001b.

Collins, W. D., Rasch, P. J., Boville, D. A., Hack, J. J., McCaa, J. R., Williamson, D. K., and Briegleb, B. P.: The formulation and atmospheric simulation of the Community Atmosphere Model version 3 (CAM3), J. Climate, 19, 2144-2161, 2006.

Daligault, O.: Caractéristiques physiques des aiguilles de pin. Institut National de la Recherche Agronomique, Document PIF9112, France, 1991.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. J. R. Meteorol. Soc., 137, 553-597, 2011.

EMEP (European Monitoring and Evaluation Programme): EMEP manual for sampling and chemical analysis. EMEP/CCC-Report 1/1995 - revised. Norwegian Institute for Air Research, Kjeller, Norway, November 2001.

Folberth, G., Hauglustaine, D.A., Lathiere, J., and Brocheton, J.: Interactive chemistry in the Laboratoire de Meteorologie Dynamique general circulation model: model description and impact analysis of biogenic hydrocarbons on tropospheric chemistry, Atmos. Chem. Phys., 6, 2273-2319, 2006.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 2006.

Hauglustaine, D. A., Hourdin, F., Jourdain, L., Filiberti, M. A., Walters, S., Lamarque, J.-F., and Holland, E. A.: Interactive chemistry in the Laboratoire de Meteorologie Dynamique general circulation model: Description and background tropospheric chemistry evaluation, J. Geophys. Res., 109 (D04314), 2004, doi:10.1029/2003JD003957.

Hong, S.-Y., Dudhia, J., and Chen, S.: A revised approach to ice microphysical processes for the bulk parameterization of cloud and precipitation, Mon. Weather Rev., 132, 103-120, 2004.

Kain, J. S., and Fritsch, J. M.: Convective parameterization for mesoscale models: the Kain-Fritsch scheme- the representation of cumulus convection in numerical models, Amer. Meteor. Soc., 46, 165-170, 1993.

Klemp, J. B., Skamarock, W.C., and Dudhia, J.: Conservative split-explicit time integration methods for the compressible non-hydrostatic equations~~.~~, Mon. Weather Rev., 135, 2987-1913, 2007.

Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Blond, N., Colette, A., Coll, I., Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J. L., Pison, I., Siour, G., Turquety, S., Valari, M., Vautard, R., and Vivanco, M.G.: CHIMERE 2013: a model for regional atmospheric composition modelling, Geosci. Model Dev., 6, 981-1028, 2013.

Monteiro, A., Ribeiro, I., Techepel, O., Sá, E., Ferreira, J., Carvalho, A., Martins, V., Strunk, A., Galmarini, S., Elbern, H., Schaap, M., Builtjes, P., Miranda, A. I., and Borrego, C.: Bias correction techniques to improve air quality ensemble predictions: focus on O_3 and PM over Portugal, Environ. Model. Assess., 18, 5, 533-546, 2013.

Moro, C.: Détermination des caractéristiques physiques de particules de quelques espèces forestières Méditerranéennes. Institut National de la Recherche Agronomique, Document PIF2006-06, France, 2006.

Nenes, A., Pandis, S.N., and Pilinis, C.: ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, Aquat. Geochem., 4, 123-152, 1998.

Noh, Y., Cheon, W. G., Hong, S. Y., and Raasch, S.: Improvement of the k-profile model for the planetary boundary layer based on large eddy simulation data, Bound.-Lay. Meteorol., 107, 401–427, 2003.

Pay, M. T., Piot, M., Jorba, O., Gassó, S., Gonçalves, M., Basart, S., Dabdub, D., Jiménez-Guerrero, P., and Baldasano, J. M.: A full year evaluation of the CALIOPE-EU air quality modeling system over Europe for 2004, Atmos. Environ., 44, 3322-3342, 2010.

Pun, B. K., Seigneur, C. and Lohman, K.: Modeling secondary organic aerosol formation via multiphase partitioning with molecular data. Environ. Sci. Technol., 40, 4722-4731, 2006.

Ratola, N. and Jiménez-Guerrero, P.: Combined field/modelling approaches to represent the air-vegetation distribution of benzo[a]pyrene using different vegetation species, Atmos. Environ., 106, 34-42, 2015.

San José, R., Pérez, J. L., Callén, M. S., López, J. M., and Mastral, A.: BaP (PAH) air quality modelling exercise over Zaragoza (Spain) using an adapted version of WRF-CMAQ model, Environ. Pollut., 183, 151-158, 2013.

Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O., Barker, D. M., and Duda, M. G.: A description of the Advanced Research WRF Version 3. NCAR technical note NCAR/TN20201c475+STR, http://www.mmm.ucar.edu/wrf/users/docs/arw v3.pdf, 2008.

Szopa, S., Foret, G., Menut, L., and Cozic, A.: Impact of large scale circulation on European summer surface O_3 and consequences for modelling forecast., Atmos. Environ., 43, 1189-1195, 2009.

Torseth, K., Aas, W., Breivik, K., Fjaeraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009, Atmos. Chem. Phys., 12, 5447–5481, 2012.

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and Tarrasón, L.: Evolution of NOx emissions in Europe with focus on road transport control measures, Atmos. Chem. Phys., 9, 1503-1520, 2009.