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Modelling benzo[a]pyrene in air and vegetation for different land uses and assessment of increased health risk in the Iberian Peninsula

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Abstract The ability of the modelling system WRF+CHIMERE implemented with high spatial and temporal resolution over the Iberian Peninsula (IP) to represent the levels of benzo[a]pyrene (BaP) in air and vegetation was tested in areas where different land uses are observed. Biomonitoring data available on the levels of polycyclic aromatic hydrocarbons (PAHs) in pine needles from the IP were used to estimate the atmospheric concentrations of BaP and, at the same time, fuelled the comparison of the vegetation representations given by the model. A total of 70 sites were sampled, including urban, industrial, rural and remote locations, which revealed different performances of the method for air and vegetation concentrations of BaP. The validation of this chemistry transport model (CTM) was complemented with the data available from the European Monitoring and Evaluation Programme (EMEP) air sampling network. This, in association with a quantitative risk assessment (QRA) method, allowed the estimation of the increased risk of lung cancer due to exposure to BaPs in the IP for three target values set by the European Union.

Keywords Polycyclic aromatic hydrocarbons · Modelling · Land use · Biomonitoring · Human health

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) can be found in the atmosphere associated with the gaseous or the particulate phases (Kiss et al. 2001; Lammel et al. 2009) and also in other environmental matrices such as soil, water, sediment or vegetation (Wild and Jones 1995; Chen et al. 2004; Ratola et al. 2010a, b). These chemicals raise concern among the scientific community and have been widely studied due to their carcinogenic and mutagenic properties. Having high lipid solubility, PAHs are absorbed in the lung tissue, skin, breasts or intestines, posing risks to the human health (Maron and Ames 1982; Howard et al. 1995; Kim et al. 2013). Benzo(a)pyrene (BaP), with a five-aromatic ring molecular structure (and thus present in the atmosphere mainly as particulate matter) is possibly the most studied of this family of compounds, and the European Commission (Directive 2004/107/EC, amended by Regulation 219/2009) defined an average limit of 1 ng m^{-3} of BaP over 1 year as a reference for PAH air quality standards (European Commission 2009). Although legal limits for atmospheric PAHs are scarce, some guidelines have been presented by studies in literature that can help in the assessment of their harmful potential (Nisbet and LaGoy 1992; Delgado-Saborit et al. 2011; Butterfield and Brown 2012).

According to literature on PAHs, their presence in the atmosphere represents only 0.5 % of the total environmental load (Maliszewska-Kordybach 1999). Wild and Jones (1995) reported that airborne PAHs represent only 4 % of total anthropogenic emissions emitted in a year in the UK. These evidences suggest that the atmosphere is not a sink for these compounds but rather a privileged mean for their transport, transformation and subsequent deposition on the Earth surface, and the study of such processes is as crucial as it is difficult. To fill the gaps still existing in the understanding of the life cycles of these persistent compounds, the use of chemistry transport models (CTMs)

can complement existing field sampling campaigns (Jiménez-Guerrero et al. 2008; Morville et al. 2011), with implications in the areas of meteorology, atmospheric chemistry and even climate change (Matthias et al. 2008; Gasic et al. 2010; Kallenborn et al. 2012; Jiménez-Guerrero et al. 2013). The modelling methods currently applied use very simple mass balance techniques or have deterministic approaches, reflecting the complexity to characterise adequately the processes involving these contaminants. Such limitations call for more experimentally based data and if possible designing multi-matrix studies (Mariussen et al. 2008) and their combination with modelling approaches in order to address the problem properly (Jakeman et al. 2006; Pistocchi et al. 2010).

This is why the use of alternative ways to include field-sampling data to validate the model urges. For instance, biomonitoring using plant species has been used to evaluate the levels of PAHs in the environment since the late 1980s (Eriksson et al. 1989). Pine trees have a worldwide presence, and the Iberian Peninsula is no exception. Consequently, there is a great potential to set up small- to large-scale spatial studies, enhanced by the life span of the needles (up to several years, depending on the species), which continuously accumulate organic pollutants (Lehndorff and Schwark 2009). However, studies reporting a wide geographic distribution of accumulation patterns of PAHs using coniferous needles are scarce and use different approaches (Weiss et al. 2000; Lehndorff and Schwark 2004; Hwang and Wade 2008; Augusto et al. 2010; Amigo et al. 2011). Even fewer are those dealing with the estimation of air-vegetation partitioning phenomena (St-Amand et al. 2009a, b).

Thus, combining field data from biomonitoring campaigns (or atmospheric sampling networks such as the European Monitoring and Evaluation Programme, EMEP) and CTMs can be a way to obtain reliable estimates of the air-vegetation loads of PAHs, as well as a more comprehensive insight on their geographical and temporal distribution. Following a concept using the WRF+CHIMERE modelling system presented by the same authors (Ratola and Jiménez-Guerrero 2015), the main objective of this work was to evaluate if field and modelling approaches can accurately represent the levels of BaP in different land uses (urban, industrial, rural and remote) and if there are important differences influenced by those areas, together with an evaluation of the hazardous potential of atmospheric BaP in the IP, concerning the risk of lung cancer.

Experimental section

Target area and field-based datasets

Located in the southwesternmost part of Europe, the Iberian Peninsula (IP) has an area of almost 600,000 km^2 and the majority of its 55 million inhabitants are distributed along the coastlines, with the exception of Madrid, Seville and Zaragoza. Forests predominate in the north, but are present throughout the territory, in a similar pattern with mountainous areas. Numerous rural activities can also be found almost everywhere. This socio-geographic layout is ideal to portray the potential differences between different land uses in terms of the atmospheric behaviour of contaminants of concern such as BaP.

Detailed information on the sampling set-up and on the available field-based results used in this study can be found elsewhere (Ratola et al. 2006, 2009, 2010a, 2012; Ratola and Jiménez-Guerrero 2015). In brief, two sets of field data describing the concentrations of BaP were considered in this work: the levels of BaP found in biomonitoring campaigns performed in 2007 using pine needles and in the EMEP air monitoring stations available in the IP. In the first case, pine needles were collected from 70 sites (33 in Portugal and 37 in Spain), covering urban, industrial, rural and remote locations. In the second case, EMEP data was gathered in weekly or monthly averages from the available station in the IP, within our chosen timeframe (2006–2010): Niembro, Campisabalos, O Saviñao, Víznar, Peñausende, Barcarrota, Zarra, San Pablo de los Montes, Mahón and Els Torms. These locations can be considered as descriptors of regional background concentrations.

BaP atmospheric levels from pine needles

To compensate for the current information scarcity in the IP, a methodology presented by St-Amand and co-workers (2007, 2009a, b) was followed to estimate atmospheric BaP levels for all biomonitoring sites considered in this work, using the concentrations found in the respective pine needles. Details of these calculations can be found in Ratola and Jiménez-Guerrero (2015). In brief:

$$\mathrm{Ca} = \mathrm{Cp} + \mathrm{Cg} \quad (1)$$

with

$$\mathrm{Cp} = (\mathrm{Cvp} \times m)/(A \times \mathrm{v_p} \times t) \quad (2)$$

and

$$\mathrm{Cg} = (\mathrm{Cvg} \times m)/(A \times \mathrm{v_{gt}} \times t) \quad (3)$$

where Ca, Cp, Cg—total, particulate and gas-phase (respectively) concentrations of the target compound in air (ng m^{-3}); Cvp, Cvg—contribution of particle-bound and gaseous deposition (respectively) to the total concentration in vegetation (ng g^{-1}); m—dry weight of pine needles (g); A—total surface area of pine needles (m^2); $\mathrm{v_p}$—particle-bound deposition velocity (m h^{-1}); $\mathrm{v_{gt}}$—net gaseous transfer velocity (m h^{-1}); t—environmental exposure time of pine needles, estimated from April 15 (considered as the day the needles sprung out) to the sampling day (h). Gas-phase contribution

for BaP is negligible; hence, ø≈1 and v_p can be obtained by equation 2. Since no concomitant atmospheric measurements were available, v_p could not be calculated for our samples, a general value for the deposition velocity for BaP over a coniferous forest canopy reported by Horstmann and McLachlan (1998) was used: 2.196 m h^{-1}.

Set-up and validation of the modelling approach

The Weather Research and Forecasting (WRF, Skamarock et al. 2008)+CHIMERE (Menut et al. 2013) modelling system with a resolution of 9 km for the entire IP was used in this case, coupled to BaP emissions given by EMEP (Vestreng et al. 2009). The exchanges gas/particle for BaP are already addressed in the current version of CHIMERE. BaP is introduced in the model as three different types of species at the same time: primary, semi-volatile (the gas-particle exchange is governed by dynamic balance between the two phases according sharing constants defined in EMEP 2005) and reactive. In this latter sense, BaP and its degradation by OH radicals, which represents over 99 % of the degradation path for BaP (Bieser et al. 2012) has been included in the model. BaP is degraded in the gas phase by first-order kinetics relative to the OH radical. The kinetic is constant if 5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for BaP. For further details on the model options, the reader is referred to Menut et al. (2013).

The model system was run and evaluated for a simulation covering the years 2006 to 2010 on an hourly basis. Further explanation of the modelling set-up, the parameterisations used and the validation strategy are reported in Ratola and Jiménez-Guerrero (2015). In brief, for the validation procedures, data from the EMEP monitoring stations were used (Torseth et al. 2012). A number of statistical parameters were tested for both canopy deposition and atmospheric levels. For instance, spatial correlation coefficient (r), root mean square error (RMSE) and mean bias (MB) are commonly used by modellers and have thus been used according to the criteria set for the Europe domain by Pay et al. (2010). In addition, according to Boylan and Russell (2006), the mean normalised bias error (MNBE) for each model-observed pair by the observation is helpful but, on the other hand, may present some problems when evaluating particulate matter. As an alternative, they suggest the use of the mean fractional bias (MFB) and the mean fractional error (MFE). In these cases, the model performance target would be met when MFE ≤50 % and MFB ±30 %, and the model performance criterion when MFE ≤75 % and MFB ≤±60 %. As such, these criteria were chosen to supply the metrics for the evaluation of BaP by the WRF+EMEP+CHIMERE system. Annual and seasonal mean statistics are processed, with winter corresponding to December, January and February (DJF); spring to March, April and May (MAM); summer to June, July and August (JJA) and autumn to September, October and November (SON).

With the objective of reaching the best approximation of atmospheric BaP concentrations through modelling approaches, the multiplicative ratio bias-correction technique described by Borrego et al. (2011) has been applied to act as a reference pseudo-reality to estimate the most accurate vegetation-to-air conversion method. The correction factor employed is the quotient between the additions of observed and modelled concentrations at a given hour of the n previous days, with a recommended 4-day training period (n=4, Borrego et al. 2011; Monteiro et al. 2013). Nonetheless, considering that the EMEP database only provides results on a weekly basis, it was decided in the current study to have a 4-week training period in order to obtain a sufficiently long timeframe to gather adequate statistics, yet not as much as to mask potential seasonal patterns.

Results and discussion

BaP model estimations for vegetation and air

The model estimation provided by CHIMERE for the deposition of BaP over vegetation is a function of BaP concentration in each site, and the mean annual BaP deposition levels reported by Ratola and Jiménez-Guerrero (2015) for the IP showed the highest mean depositions for the northwest, reaching over 50 ng g^{-1} yr^{-1} in some areas of Galicia and Asturias. On the contrary, in parts such as the north and central plateaus, and the Ebro (northeast), Guadalquivir and Guadiana (south) river valleys, the BaP incidence was very low, likely a reflection of the importance of the presence of vegetation more strongly than of potential emission sources. This "forest filter effect" is recognised by scientists and adds to the conclusion that they act as sinks of atmospheric semi-volatile organic contaminants (Maddalena et al. 2003). Consequently, it is not surprising that in a depiction of deposition over vegetation canopies, forested areas reveal more incidence than arid ones.

When the model estimates the BaP concentrations in the atmosphere, the spatial pattern is actually not that different from the vegetation simulations. However, the key influence of local emissions can be ascertained in this case, as heavily urbanised areas such as Barcelona or Madrid present a high incidence, not appreciable due to the more limited vegetation over urban land uses. As seen in Fig. 1, results reveal a tendency for seasonality. In the colder months (winter—DJF—and autumn—SON), sources of PAHs like traffic and building heating are increased and this is reflected not only by the field measurements (Ratola et al. 2010a) but also by the models,

with strong positive anomalies with respect to the annual mean in the areas with the most incidence of atmospheric BaP (NW Spain and western coast of Portugal). The highest deposition concentrations registered using pine needles as the biomonitoring matrix and also the highest atmospheric concentrations simulated by the model were found in urban and industrial settings, mainly distributed along the northwestern coast of the Iberian Peninsula (as also indicated in previous works by Amigo et al. (2011); Ratola et al. (2012)), followed by rural and remote areas. This again reflects the accumulation of anthropogenic sources of BaP involving combustions in the most populated areas of the IP.

The results of the validation of the CTM results against the available field-based air quality data available from EMEP stations after the removal of the bias were reported elsewhere (Ratola and Jiménez-Guerrero 2015), showing overall mean fractional biases (MFB) below ±25 % for all stations except Peñausende (MFB=+43 %), which indicate very accurate comparisons. These low biases suggest that the atmospheric levels of BaP are being correctly estimated by the CTM.

Modelling land use influence using biomonitoring campaigns

Comparison for vegetation levels

The modelled deposition over vegetation was compared to data from BaP levels in pine needles obtained in field sampling campaigns in the IP (Ratola et al. 2009, 2010a, 2012). Table 1 presents the main statistical validation parameters separated by each of the four land uses considered for the biomonitoring sampling sites (urban, industrial, rural and remote).

Results show that the modelling approach has in general a good indication of an overall good capacity to describe the vegetation's uptake of BaP, in comparison with the biomonitoring data. There are, however, some facts worth mentioning regarding the behaviour for each site type (or land use pattern). In industrial and remote areas, the model is likely to overpredict the concentrations in all seasons except MAM for the former (Table 1), with MFBs up to +47 % and biases up to 2.27 ng g^{-1}. On the other hand, rural and urban areas are

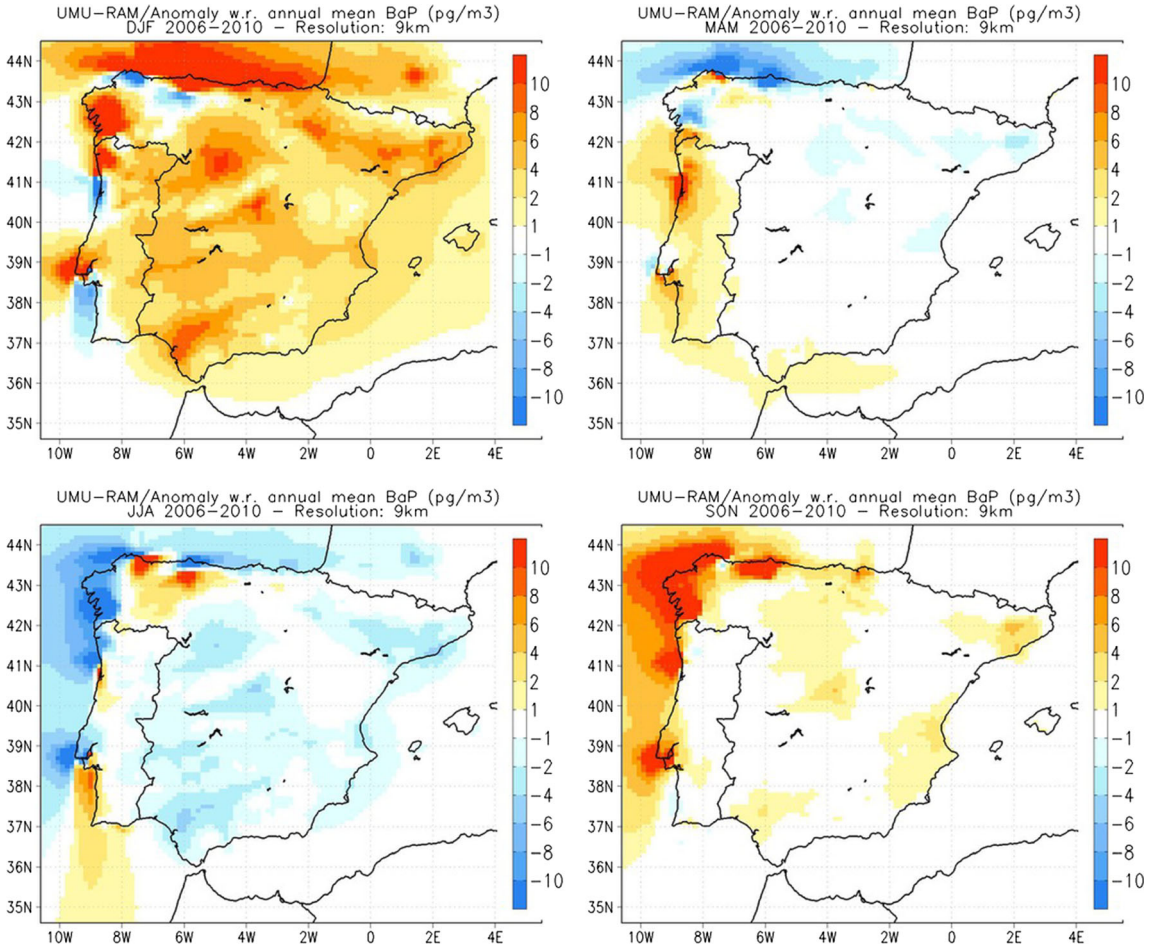

Fig. 1 Seasonal differences (pg m^{-3}) with respect to the annual mean concentration in the atmosphere: (from *top-down* and *left-right*): winter (*DJF*), spring (*MAM*), summer (*JJA*) and autumn (*SON*) climatologies for the period 2006–2010

Table 1 Seasonal evaluation of modelling results (over vegetal canopies) against biomonitoring (pine needles) data according to the site type

	Industrial (N=12)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.987	0.941	0.842	0.841
0.731	MFB (%)	27.91	45.17	−15.24	34.58
	RMSE (ng g^{-1})	1.60	2.27	0.66	1.42
	Bias (ng g^{-1})	0.89	0.38	−0.52	1.74
	Mean OBS (ng g^{-1})	2.54	4.47	2.25	1.92
	STD OBS (ng g^{-1})	2.03	4.38	1.40	1.13
	Mean MOD (ng g^{-1})	4.49	4.85	1.73	2.73
	STD MOD (ng g^{-1})	3.02	3.53	0.88	2.00
	Remote (N=2)	DJF	MAM	JJA	SON
Temporal R	Spatial R	N/A	N/A	N/A	N/A
0.841	MFB (%)	36.36	46.60	38.80	35.57
	RMSE (ng g^{-1})	0.59	0.59	0.25	0.89
	Bias (ng g^{-1})	0.56	0.59	0.25	0.72
	Mean OBS (ng g^{-1})	0.90	0.48	0.44	0.99
	STD OBS (ng g^{-1})	0.15	0.10	0.22	0.15
	Mean MOD (ng g^{-1})	1.46	1.07	0.69	1.71
	STD MOD (ng g^{-1})	0.41	0.01	0.15	0.90
	Rural (N=31)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.898	0.412	0.561	0.798
0.788	MFB (%)	−1.32	−1.60	−33.62	19.50
	RMSE (ng g^{-1})	1.18	1.07	0.57	0.54
	Bias (ng g^{-1})	−0.05	−0.34	−0.63	0.49
	Mean OBS (ng g^{-1})	2.04	2.32	1.35	1.31
	STD OBS (ng g^{-1})	1.35	1.85	0.87	0.82
	Mean MOD (ng g^{-1})	1.70	1.98	0.72	1.52
	STD MOD (ng g^{-1})	1.05	1.01	0.39	1.00
	Urban (N=27)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.559	0.589	0.401	0.493
0.687	MFB (%)	−18.03	11.20	−40.08	−24.67
	RMSE (ng g^{-1})	1.20	1.81	0.47	1.78
	Bias (ng g^{-1})	−0.09	0.21	−0.30	−0.70
	Mean OBS (ng g^{-1})	1.52	1.97	0.93	2.03
	STD OBS (ng g^{-1})	0.81	1.93	0.35	2.01
	Mean MOD (ng g^{-1})	1.70	2.18	0.63	1.48
	STD MOD (ng g^{-1})	1.49	2.09	0.47	1.05

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, *MOD* modelled concentrations, *STD* standard deviation, *R* correlation coefficient, *N* number of sampling sites

generally underestimated by the model, but with lower MFBs (from −1.32 to −40.08 %). The summer months are those with the highest biases (negative) in these locations but, in this case, since we are considering the deposition upon vegetation, may not be a clear suggestion of the site type influence. In fact, most industrial and remote areas considered are also associated with strongly forested areas nearby, and thus, the aforementioned over-prediction in the BaP levels can derive from this. In contrast, urban and rural areas may have a stronger influence from local emissions, which cannot be acknowledged from the results of canopy deposition. Figure 2 (top) reflects the problems of the model to adjust to the different land uses, although the inaccuracies found can be considered not particularly significant, except for remote sites.

Table 1 also shows that the RMSE is in most cases below 1.2 ng g^{-1} in all seasons, which implies a good approximation between model and biomonitoring data, a close approach of the model to the levels obtained from pine needles. This is in line with the temporal correlation coefficients found for the four land uses (from 0.687 in urban to 0.841 in remote sites). It should be remarked that only two sites are available for remote locations, and this is why it was impossible to establish a spatial correlation in this case. For the other sites, clearly the best spatial response of the model was given for industrial areas, with correlations between 0.841 and 0.987, for autumn and winter, respectively. As mentioned before, the proximity to forested terrains may be important for this strong affinity. The worst results are obtained for the urban sites (R from 0.401 in summer to 0.589 in spring). These sites are scattered throughout the IP, both in areas with heavy forestry and in more arid regions, and this can affect the representation of a spatial trend on canopy deposition.

So, as expected, given the good performance of the model, the modelled results follow the trend already reported for the biomonitoring campaigns. For the 16 EPA PAHs, Ratola et al. (2010a) and Amigo et al. (2011) observed that the urban and industrial sites have the predominant mean PAH incidence, followed by the rural sites, and with the remote sites showing clearly the lowest levels. Similar features were also mentioned in other parts of the world (Tremolada et al. 1996; Lang et al. 2000; Piccardo et al. 2005; Tian et al. 2008). However, for higher molecular weight PAHs (such as BaP), linked predominantly to traffic, industrial activities and other combustion processes (Orecchio et al. 2008; Singh et al. 2008), the highest levels were seen precisely in the industrial areas. Table 1 shows this tendency, with mean BaP concentrations between 1.92 and 4.47 ng g^{-1} for autumn and spring, respectively. Urban and rural sites have similar incidences (up to 2.32 ng g^{-1}), and the remote areas clearly present the lowest levels (below 0.99 ng g^{-1}). Interestingly, the seasonal pattern usually seen for PAHs (higher incidence in winter and lower in summer) is not entirely verified for BaP. In fact, for each site type, there is a different trend, although overall, there is a higher proportion of the BaP load in the colder months (Table 1). Being a particulate material, this contaminant is probably more prone to external aggression (mainly meteorological) that will remove it from the surface of the needles, regardless of other seasonal tendencies (Yang et al. 2007).

Some geographic differences were reported in the characteristics of pine needles, which is prone to affect their uptake

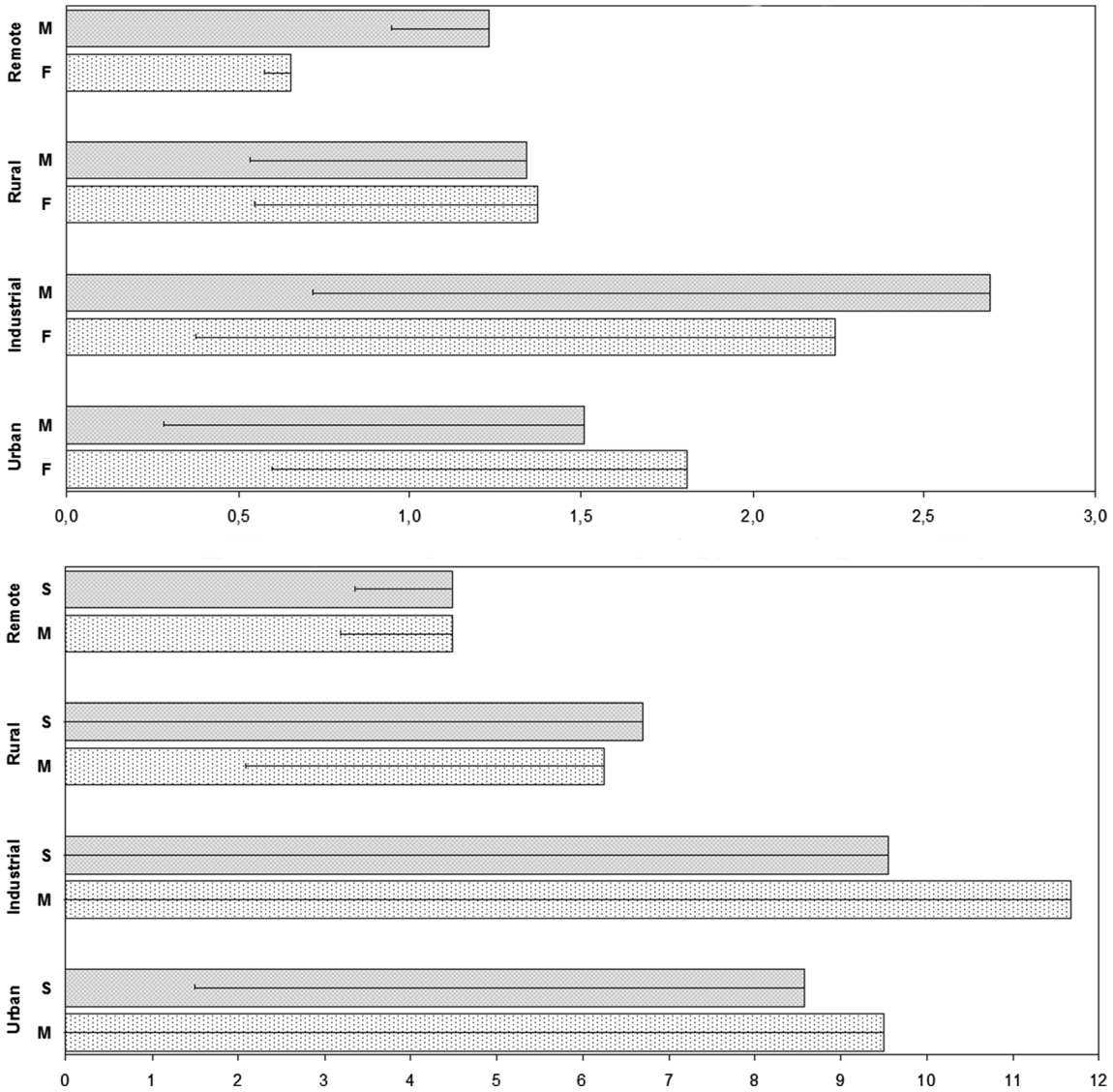

Fig. 2 (*Top*) Deposition levels (ng g^{-1}) on pine needles according to the site types (*F* field, *M* CTM modelling). (*Bottom*) Mean atmospheric concentrations (pg m^{-3}) as estimated by CTM modelling (*M*) and air-vegetation conversion (*S*) by St-Amand et al. (2007, 2009a, b). *Black lines*: standard deviation

capacity. According to Anfodillo et al. (2002) and Martínez-Vilalta et al. (2009), this evidence is particularly seen in latitudinal and altitudinal gradients where the influence on climatic patterns is stronger than in longitudinal frameworks.

Comparison for air levels

Considering that the CTM draws a trustful image of the atmospheric levels of BaP, it is plausible that the dataset created can be employed to assess the performance of an air/vegetation estimation starting with the biomonitoring results available for each of the four land uses considered in this study (urban, industrial, rural and remote). Thus, the pseudo-reality model results from WRF+CHIMERE were taken as a reference to validate a conversion of pine needles into atmospheric concentrations, based on the methodology mentioned in "BaP atmospheric levels from pine needles" section.

According to Table 2, the BaP concentrations determined by the estimation from pine needles follow the trend observed for the canopy deposition, with an industrial>urban≈rural> remote distribution of concentrations (min 2.77 pg m^{-3} for remote sites in summer and max 22.5 pg m^{-3} for industrial sites in winter and spring). In this case, the typical seasonal trend observed for PAHs in the atmosphere is verified, with the BaP incidence predominating in winter and showing the lowest levels in the warmest months. However, the results observed for the mean CTM concentrations indicate a slightly different pattern in terms of land uses, as the urban sites reach higher levels than the rural ones. Figure 2 (bottom) gives a clear indication of this fact (mean 9.5 pg m^{-3} for urban against

6.2 pg m^{-3} for rural), suggesting that CTM estimations reflect with slightly more accuracy the common atmospheric features that the indirect estimation from pine needles. Nevertheless, the MFB are below 20 % for the majority of the site types and corresponding seasons, with the exceptions all complying with the model performance criterion of MFB≤±60 % (Boylan and Russell 2006). The lowest MFBs are obtained for the rural areas (between −8.50 and 12.37 %) and the highest for the industrial ones. The multitude of emitting sources in the latter case can make its representation more difficult, as pine needles may not be able to fully express such diversity, compared to a direct atmospheric measurement.

The temporal and spatial correlation coefficients disclose tendencies comparable to the modelled canopy deposition (R from 0.556 to 0.842 and from 0.409 to 0.978, respectively, see Table 2). Still, the representation of the urban sites shows an improvement in both correlations. Again, the dispersion of these sites through areas of strong incidence of vegetation and more arid locations allows the atmospheric simulations to be more correct. Plus, the CTM can, in this case, describe

Table 2 Results from the comparison of BaP concentrations in air obtained by the chemistry transport model simulations and those estimated from pine needle levels by St-Amand et al. (2007, 2009a, b), grouped by site type

	Industrial (N=12)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.921	0.978	0.813	0.642
0.556	MFB (%)	15.03	50.77	19.70	−9.12
	RMSE (pg m^{-3})	9.89	6.82	5.01	15.06
	BIAS (pg m^{-3})	3.98	6.81	1.93	−4.16
	Mean St. Amand (pg m^{-3})	22.53	22.54	12.06	6.34
	STD St. Amand (pg m^{-3})	20.63	21.31	8.35	3.64
	Mean CTM (pg m^{-3})	15.11	14.22	6.86	10.49
	STD CTM (pg m^{-3})	14.65	13.33	6.21	10.25
	Remote (N=2)	DJF	MAM	JJA	SON
Temporal R	Spatial R	N/A	N/A	N/A	N/A
0.842	MFB (%)	10.34	−36.63	−9.42	41.15
	RMSE (pg m^{-3})	0.56	1.92	0.71	2.18
	Bias (pg m^{-3})	0.79	−1.86	−0.09	1.79
	Mean St. Amand (pg m^{-3})	8.04	4.05	2.77	5.28
	STD St. Amand (pg m^{-3})	1.32	0.81	1.42	0.80
	Mean CTM (pg m^{-3})	5.68	5.91	2.85	3.49
	STD CTM (pg m^{-3})	2.23	1.51	0.42	0.97
	Rural (N=31)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.409	0.464	0.413	0.668
0.662	MFB (%)	3.94	2.28	12.37	−8.50
	RMSE (pg m^{-3})	14.36	9.87	3.16	3.93
	Bias (pg m^{-3})	8.03	2.97	0.82	−0.50
	Mean St. Amand (pg m^{-3})	18.97	17.05	7.20	4.99
	STD St. Amand (pg m^{-3})	18.63	14.41	4.09	3.41
	Mean CTM (pg m^{-3})	9.07	8.05	3.84	5.48
	STD CTM (pg m^{-3})	3.30	7.87	3.65	4.05
	Urban (N=27)	DJF	MAM	JJA	SON
Temporal R	Spatial R	0.519	0.795	0.590	0.959
0.796	MFB (%)	−17.92	20.30	−14.41	1.93
	RMSE (pg m^{-3})	12.96	8.54	4.90	4.06
	Bias (pg m^{-3})	−4.53	1.23	−1.74	0.16
	Mean St. Amand (pg m^{-3})	11.98	13.01	4.51	8.44
	STD St. Amand (pg m^{-3})	7.73	14.14	2.23	8.22
	Mean CTM (pg m^{-3})	13.65	10.69	4.79	8.27
	STD CTM (pg m^{-3})	13.46	10.48	4.77	8.02

Modelling results are considered as the pseudo-reality 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, *R* correlation coefficient, *MFB* mean fractional bias, *RMSE* root mean square error

up to a certain point the differences of BaP loads in diverse land use scenarios. Further studies are due, however, to establish a closer affinity in the assessment of land use patterns and the neighbouring vegetation types in each area.

Assessment of increased health risks

If these methods intended to describe the presence and behaviour of priority pollutants are continuously enhanced, the benefits can be remarkable, even at the level of the human health issues. Thus, it is also the goal of this study to provide an example of how these tools can help in the assessment (and correction) of human health potentially hazardous effects.

When the European Union set their Target Value in the Directive 2004/107/EC, a quantitative risk assessment (QRA) method was based on different studies, such as Andersen et al. (1982), Lindstedt and Sollenberg (1982) or RIVM (1989). These studies focused on the increased risk of lung cancer due to industrial exposure to PAHs. This QRA method is laid out in the European Union's "Ambient air pollution by polycyclic aromatic hydrocarbons (PAH)" Position Paper (European Union 2001). Using this method and the World Health Organisation (World Health Organisation 2000) unit risk of lung cancer (8.7×10^{-5} BaP m^{-3} for lifetime exposure) estimate for PAH compounds, the European Union calculated the increased risk for three possible target values: (1) target value of 0.01 ng m^{-3} with an associated increased risk of 1×10^{-6}; (2) target value of 0.1 ng m^{-3} (increased life-time risk of 1×10^{-5}); and (3) target value of 1 ng m^{-3} with an associated increased risk of 1×10^{-4}.

Based on the health evidence and acceptance that the upper limit of the additional lifetime risk should be less than 1×10^{-4}, the European Union decided on a target value for the annual mean concentration of BaP to be 1 ng m^{-3} (Butterfield and Brown 2012).

As seen in Fig. 3, this target value of 1 ng m^{-3} (associated to an increased life-time risk of lung cancer of 1×10^{-4}) is only met in northwestern Spain (precisely, in some areas of Galicia with an important presence of carbon power plants). While some areas exceed the target value of 0.1 ng m^{-3} with associated increased risk of 1×10^{-5} for lung cancer, lifetime exposure (mainly in the largest Portuguese cities, Lisbon and Porto, and in some areas in northern Spain), the rest of the peninsula does not exceed the 0.1 ng m^{-3} target value (values under 0.1 ng m^{-3} in western Iberian Peninsula and 0.01 ng m^{-3} in the Spanish eastern coast). This involves increased risks of lung cancer under 1×10^{-5} and 1×10^{-6}, respectively.

Conclusions

The shortage of atmospheric measurements of BaP over the IP (and, in general, over Europe) has forced to apply a methodology combining biomonitoring samples and modelling results in order to characterise the levels of BaP over the target area, and to study the different abilities of the model to reproduce ground-level concentrations over different land uses in the IP. The results indicate a very good performance of the model over all types of land uses, but with a tendency of model to over-predict the concentrations in all seasons over industrial and remote areas. At the same time, the best spatial

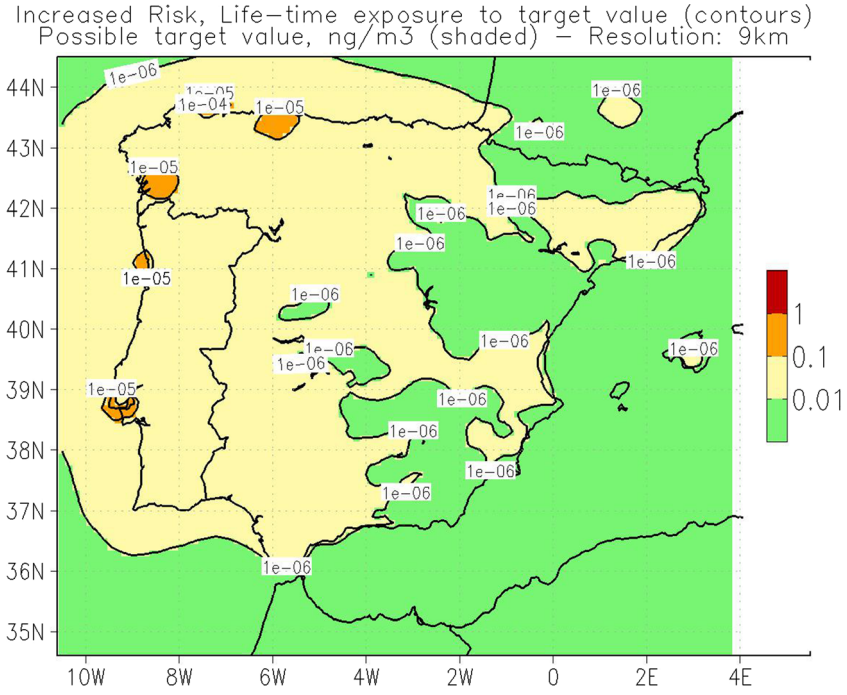

Fig. 3 Exceedances of the possible target values (*shaded*, ng m^{-3}) and associated increased risk of lung cancer, lifetime exposure to the target value (*contours*), as defined by the quantitative risk assessment included in Butterfield and Brown (2012)

response of the model was given for industrial areas, due to the proximity of large emitting areas. On the other hand, the worst results are obtained for the urban sites, but those land uses are scattered throughout the IP. Moreover, an analysis of the increased risk of lung cancer due to the atmospheric exposure to BaP has been performed using modelling data, with an increased lifetime risk of lung cancer of 1×10^{-4} for some areas of northwestern Spain, where the 1 ng m^{-3} as annual mean is exceeded.

Simulating a large period of time (2006–2010) adds a climatic perspective to the BaP assessment on a regional scale, in this case, covering the IP territory. Overall, the relevance of this work forecasts the increasing use of pine needles (and other vegetation species) in a comprehensive study of the behaviour of semi-volatile organic compounds (SVOCs). Health issues associated to these chemicals are extremely important and the monitoring of possible effects derived from the exposure levels is a field that can be explored combining field and model approaches, aiming to set further air quality guidelines.

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