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Can biomonitors effectively detect airborne benzo[a]pyrene? An evaluation approach using modelling

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

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. 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 ($\mu g\ m^{-3}\ s^{-1}$) 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 3.75º x 2.5º 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. 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 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 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-adjustment technique has been applied following the methodology of Borrego et al. (2011). The 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".

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

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	LONG	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	LONG	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**

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