

Response to:

Interactive comment on “Can we use modelling methodologies to assess airborne benzo[a]pyrene from biomonitors? A comprehensive evaluation approach” by N. Ratola and P. Jiménez-Guerrero

Anonymous Referee #2

NOTE: The authors deeply appreciate the evaluation made by the referee to the manuscript and hope to have responded successfully to all the valuable comments and suggestions posed. We believe that the effort and changes we introduce in our revision will allow the manuscript to meet all the aspects mentioned below in a successful manner.

Received and published: 25 November 2015

1. The paper addresses the question of whether pine needles can be used as a proxy for measurement of atmospheric BaP. This is an interesting topic, and one relevant to the field of atmospheric chemistry and the study of atmospheric PAHs in particular.

2. While the method of biomonitoring of BaP is not novel, this detailed assessment of biomonitoring campaigns against modeled and measured atmospheric BaP is an important conceptual step to take.

3. The conclusion reached, that biomonitoring is effective for detecting the presence and spatial distribution of BaP, is significant and quantitatively investigated. The spatial distribution of BaP being reflected by biomonitoring is indeed supported by the results, though at varying degrees depending on the season.

4. The scientific methods are presented in a clear manner. Specific comments on the methodology:

a) A model was used as pseudo-reality, after being calibrated to measurements. This use of the calibrated model presents no problem provided that the model values are independent of the biomonitor-calculated values that they are compared to. The authors acknowledge that the pine needle-based estimates that rely on deposition velocities are therefore connected to the model estimates because the model also uses a deposition velocity value in the process of calculating concentrations. The authors argue that since the model does well in comparison to EMEP air measurements, that this model's deposition velocity is appropriate for the Iberian Peninsula. I believe that the comparison's reliance on this argument, and the independence of the model calculations and vegetation-based estimates, should be discussed further.

Response: The argument in which this work relies on is not exactly captured in the reviewer's comment. The adequacy of the model's deposition velocity for the Iberian Peninsula is assessed by comparing the model deposition with the measured deposition on the pine needles. So there is a direct evaluation of the deposition velocity against observations. The accuracy of the model to capture the air concentrations is evaluated against EMEP air measurements. Hence, our argument is: since the model correctly captures air concentrations and deposition (which are assessed independently one from the other), we can use the modeled air concentrations as a reference to evaluate the fitness of the different vegetation-air conversion approaches.

This is roughly stated in the text. However, the text of the revised version has been modified in order to enlighten the discussion. Actually, some of the response to comment 5 also complements this issue.

b) There are many sources of uncertainty in the EMEP measurements, the modeled concentrations, the biomonitored concentrations, and the methods of intercomparison. I wonder how these uncertainties limit the conclusions of the evaluation of the biomonitoring. The authors should at least comment on how the uncertainties involved qualitatively affect the evaluation, if not quantitatively estimate the effect of the uncertainties.

Response: A detailed description of the uncertainty associate to each step of the process is, in our opinion, beyond the scope of this manuscript due to its intrinsic complexity. However, we can characterize the main source of uncertainty in our global process. As stated by San José et al. (2013) (reference included in the manuscript), the main source of uncertainty comes from the emission inventories for PAHs. In general, this uncertainty was estimated to be within a factor of 2 to 5 (Berdowski

et al., 1997). This uncertainty is much larger than any other uncertainty associated to the validation process.

This comment and some more discussion on the subject were included in the revised version of the manuscript, as well as the following references:

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 für Umwelt, Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungsbericht 104 02 672/03. TNO, Apeldoorn, The Netherlands, 1997.

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.

5. Overall, I believe that the results support the conclusions, but I believe that there is one point that must be further discussed/explored: In the comparison of calibrated model to biomonitors, it is found that the chosen deposition velocity strongly affects the quality of the fit. With such widely varying deposition velocities from the literature (the ones used in this study varied over orders of magnitude), there is much room for the selection of the deposition velocity to match a given set of measurements. I worry that this opens the possibility for overfitting in the model-biomonitoring comparison. Would choosing the same deposition velocity for this region over a different time period yield results that are as good? Some independent reasons to choose the deposition velocity 1d for the comparison domain would strengthen the choice, but the authors write "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." (p26496 l27) Is the chosen method for biomonitors (1d) robust? Does this deposition velocity make sense over the others for a reason other than the fit with the model? As the authors note, many factors describing the atmosphere, surface, pine needles, etc. contribute to the deposition velocity. I believe that a physical argument that the deposition velocity used in method 1d is at least reasonable in an order of magnitude sense for this situation would greatly strengthen the results and conclusions.

Response: This is indeed a very important and pertinent point, as the use of biomonitors databases to assess atmospheric concentrations is a complicated task. Ideally, the air levels of semi-volatile organic compounds (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. In order to reduce this gap, other strategies such as passive sampling devices or biomonitors studies using, for instance, vegetation have been used for a number of chemicals. But obviously, 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 we present in this work derive from these type of combined studies. The deposition velocity is important in only one of the three methodologies for estimating air concentrations from vegetation (methodology which derives into approaches 1a to 1d in our work), but it allows precisely to understand the differences that may occur when conditions are changed (different species, different locations, different times of the year, different affecting sources, etc). So in fact the deposition velocities can vary in the same spot. But what models can tell us when it is impossible to have simultaneous active air and biomonitors sampling is 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). Approaches 1a to 1d are based in the same biomonitors experiment, with combined air sampling. So we consider the methodology that led to the air-vegetation partition calculations to be valid worldwide. Having no deposition velocity calculated for our sampling domain, we had to resort to the existing ones, and 1d proved to be the fittest, probably due to the fact that it was a value estimated (using modelling) for deposition on an entire coniferous canopy instead of some particular trees in a given sampling point. As a consequence, and in conclusion, a physical argument is difficult to establish. 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 continues to be as scarce as it is nowadays, the journey will be necessarily slower than we hope for. We have tried to enhance the discussion regarding this point in the text.

6. Experiments and calculations: the authors have clearly described their methodology in a way that I believe allows reproduction.

7. I believe that the authors have clearly described what is new to this work and given appropriate credit to previous studies.

8. It is unclear to me that the title reflects paper. The question that the paper is attempting to answer seems to be more along the lines of: "Can biomonitors effectively detect airborne benzo[a]pyrene? An evaluation approach using modelling"

Response: The authors agree that the suggested title reflects with more accuracy the general aim of the paper. Hence, we changed it accordingly.

9. The abstract accurately reflects the work, but needs some clarification of the final sentence. Do the authors mean to say that the model can be an effective predictor of air concentrations and values in vegetation, or something else?

Response: We intended to say that, yes, but also that the model can help us to define the best strategy to estimate air concentrations from values found in vegetation, following biomonitoring field studies. We have corrected the last sentence and hope it now reflects our intention.

10. The overall presentation of the paper is well structured and clear.

11. The language used in the paper is clear and concise, but requires some editing for English phrasing: e.g. p26497 l13: "This supposes a climatic viewpoint to the problematic of BaP..." 'supposes' should probably be replaced with 'highlights', 'displays', or similar, and 'problematic' should be replaced with 'problem'.

Response: This sentence was corrected as suggested.

12. The use of formulae is effective, and units are clearly denoted where applicable.

13. Tables: - Table 1. Are the +/- values given with the means the variances? – Table 2. Same question.

Response: These values are the respective standard deviations, and this is now reflected in the Tables.

14. The number and quality of references is appropriate for this work.

15. The supplemental information provided is appropriately detailed and clear.

Response to:

Interactive comment on “Can we use modelling methodologies to assess airborne benzo[a]pyrene from biomonitors? A comprehensive evaluation approach” by N. Ratola and P. Jiménez-Guerrero

Anonymous Referee #3

NOTE: The authors deeply appreciate the evaluation made by the referee to the manuscript and hope to have responded successfully to all the valuable comments and suggestions posed. We believe that the effort and changes we introduce in our revision will allow the manuscript to meet all the aspects mentioned below in a successful manner.

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General Comments

This manuscript describes the use of a chemical transport model (WRF+CHIMERE) to simulate airborne benzo[a]pyrene concentrations over the Iberian Peninsula. The model was driven by emissions generated by EMEP-MSC East. Ambient concentrations measured at 10 sites through EMEP were used to evaluate the airborne concentrations generated by the model. Modelled deposition was then compared to measured biomonitoring data from pine needles collected at 70 sites. The overall goals of the paper are unclear and the title does not represent its aims. A major error in the modelling framework (lack of O₃ reactivity) makes the model results unreliable. The lack of uncertainty analysis casts doubt on the applicability of the model in generating airborne concentrations and deposition.

Response: We acknowledge that the questions raised by the reviewer are very important, but we believe that by the end of our revision all the concerns and doubts will be solved.

Specific Comments

A major deficiency in the modelling framework is the error made in benzo[a]pyrene reactivity representation. Section 2.4 of the manuscript states, “This CHIMERE version includes gaseous and particulate BaP and its degradation by OH radicals, which represents over 99% of the degradation path for BaP” and this statement is referenced to Bieser et al. (2012) on p.3 of the Supplement. The relevant oxidant for benzo[a]pyrene is in fact ozone rather than hydroxyl. The relevant text in Bieser et al. (2012, p. 1399) is, “For particulate BaP, the reaction rate with ozone is 1 order of magnitude higher than other degradation processes. The main degradation path of gaseous BaP is the reaction with OH radicals. Because 99% of the total BaP is bound to particles, the reaction with ozone can be considered the only effective degradation path of BaP in the atmosphere.” Though the authors have correctly considered the particulate nature of BaP in ambient air, they have mistakenly applied the wrong degradation pathway. As a result, BaP concentrations simulated using their model are likely substantially overestimated. This error calls into question all further results described in the manuscript.

Response: The reviewer is absolutely correct regarding the degradation pathways of BaP. And indeed our model accounts for the ozone contribution in the oxidation process, but while deciding on the best arrangement to display the description of the model, this point was unintendedly left out of the text. So in the end this will have no implications in the results, but the text is now modified to explain it conveniently.

So, the following sentence has been introduced in the text (Section 2.4):

“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):

$$k = k_{\max} [\text{O}_3]/(1 + K_{\text{O}_3}[\text{O}_3]) \quad (\text{eq. 7})$$

being $k_{\max} = 0.015 \text{ s}^{-1}$ and $K_{\text{O}_3} = 2.8 \times 10^{-13} \text{ cm}^3$,

These two references were also added to the list:

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

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: O₃ and H₂O adsorption, benzo[a]pyrene degradation, and atmospheric implications. J. Phys. Chem. A 2001, 105, 4029-4041. □

Technical Corrections

General:

The authors should clarify the nature of their reported BaP values at each instance that they are mentioned: measured, modelled or bias-corrected modelled. Also, bias-corrected implies that the result is indeed "correct". Bias-adjusted is a fairer way to express this.

Response: The suggested corrections were accepted and introduced in the text and table captions. As mentioned below in response to another comment, modelled results are always presented in the bias-adjusted form, as it is now stated in the revised manuscript (Section 2.4).

Section 2.3: Why include the gaseous equation and discussion when only particulate BaP is being considered? The interested reader can refer to the cited references for full formulations.

Response: The reviewer has a point and the text was corrected to comply with the suggestion.

Line 23-24: high molecular weight, not volume

Response: Changed as suggested.

It would be easier for the reader if all formulae were put into the same form as $C_a = xxx$

Response: Corrections to the equations in question were done as suggested.

Why was a three-month average temperature used for K_{oa} calculation? How fast is equilibration between air and pine needles? Justify.

Response: Regarding the equilibrium between air and pine needles, there are still some doubts about how and if it is fully obtained. For instance, Mackay (1991) stated that the accumulation of SVOCs from the air phase by vegetation can be a slow process. Due to the high storage capacity of pine needles towards compounds with high K_{oa} (the case of BaP), equilibrium may never be completely reached due to the variable life span of the needles. Tremolada et al. (1996) concluded that it was not possible to acknowledge if "non-equilibrium" conditions or alternative pathways are involved in the bioaccumulation of these compounds in vegetation.

For this reason we decided to calculate the K_{oa} using a three-month average temperature, since it corresponded to the intervals of exposure between the collections of samples (with a seasonal periodicity for most sampling points). These use of these averages were only necessary for the calculations of Approach 3.

An explanation for our option is now included in the text.

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

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.

Section 3.1.1: The discussion of the dry deposition flux calculation should be part of the Experimental section rather than the Results

Response: The suggestion was accepted and the text changed accordingly.

Describe "corrections have been implemented" as mentioned on line 17 of p. 26490

Response: For the sake of brevity, the reader is derived to the references included in the manuscript for a detailed description of the corrections implemented in the CHIMERE model. The sentence included here was inspired by the CHIMERE manual (<http://www.lmd.polytechnique.fr/chimere/>), which also does not fully describe the corrections, but references them. So, in our opinion, the inclusion of all the formulations related to deposition over vegetal canopies would not bring an added value considering the aim of the manuscript. If further information is needed, the best resort is to corrections are thoroughly explained by the references we include. Nevertheless, we have rephrased the text.

There seems to be an implicit assumption that there is 100% uptake of deposited BaP by pine needles. How was modelled deposition flux converted to pine needle concentrations? Is the method used the reverse of that used to convert measured pine needle concentrations to those in ambient air? If so, what effect does this symmetry have on the validity of the results?

Response: The authors are aware that indeed there is an assumption that there is a full uptake by the pine needles of the deposited BaP; hence, modeled deposition flux is converted to pine needle concentration just by multiplying the modeled deposition flux times the time of exposure (equivalent for the model and the pine needle). So there is no symmetry of methods. This explanation has been included in the revised version of the manuscript.

Explain land use patterns for readers not familiar with this geographic region

Response: Some information is already presented in section 2.1, but we have tried to enhance it with some more detail.

Add uncertainty discussion/analysis to all steps in the process (model, bias adjustment to model, measurements in air, measurements in vegetation, deposition conversion to vegetation concentration) in order to constrain conclusions

Response: A detailed description of the uncertainty associate to each step of the process is, in our opinion, beyond the scope of this manuscript due to its intrinsic complexity. However, we can characterize the main source of uncertainty in our global process. As stated by San José et al. (2013) (reference included in the manuscript), the main source of uncertainty comes from the emission inventories for PAHs. In general, this uncertainty was estimated to be within a factor of 2 to 5 (Berdowski et al., 1997). This uncertainty is much larger than any other uncertainty associated to the validation process.

This comment and some more discussion on the subject were included in the revised version of the manuscript, as well as the following references:

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 für Umwelt, Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungsbericht 104 02 672/03. TNO, Apeldoorn, The Netherlands, 1997.

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.

Table 1: Specify meaning of values listed under OBS and MOD MEAN (mean plus or minus standard deviation? Standard error?)

Response: Yes, the values in this case are mean plus or minus standard deviation. This is now clarifies in the Tables.

Are modelled concentrations bias adjusted or raw?

Response: Modelled concentrations are always bias adjusted. This has been clarified in the revised version of the manuscript (in Section 2.4).

Supplement:

Modelling Experiment: What equation is used for partitioning? Does it yield the correct benzo[a]pyrene particulate fraction?

Response: A dynamical approach is used to describe the gas/particle conversion, in line with Bowman et al. (1997):

$$J_i = 1/\tau_i (G_i - G_{i_{eq}})$$

Where J_i ($\mu\text{g m}^{-3} \text{s}^{-1}$) is the absorption or desorption flux of species i ; τ_i (s) is a characteristic time of the mass transfer that is a function of particle size and the chemical properties of i ; G_i is the bulk gas-phase concentration of i and $G_{i_{eq}}$ 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).

This explanation is now included in the Supporting Information, as well as the following references:

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.

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.

Model Validation: What is the effect of the time period coverage at each measurement site? Only one covers the entire modelling period.

Response: The authors are well aware of the need for further measurements with a higher temporal coverage, as mentioned in the text. However, there is a strong limitation (not only over the Iberian Peninsula, but worldwide) for simultaneous air and vegetation measurements. So we had to rely on the best information available. We hope that this work sets a starting point for an improvement in the design of sampling campaigns and associated modeling strategies. This point of view was included in the text of the Supporting Information.

What is the EMEP sampling method? Frequency of measurement? Duration? Uncertainty in measurements? What is the effect of degradation for measurements that are weekly or monthly averages?

Response: The detailed answer to these question can be found in the "EMEP Manual for Sampling and Analysis". This manual describes all the sampling methodologies employed for each chemical and/or matrix and the recommended operation. For the EMEP sites in the Iberian Peninsula, the 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. 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 fulfilment (among others) leads to the validity of the results presented. Finally, 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).

These points are now included in the Supplementary Information text as well as the following reference:

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.

The discussion of the bias correction is unclear and should be reworded so that the reader does not need to consult the original references. What was done exactly? How much were concentrations adjusted?

Response: We applied the additive bias correction methodology as defined by Monteiro et al. (2013) (reference included in the manuscript). This bias-correction technique improves the relative mean bias (expressed as percentage) by approximately 90%. 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. Mathematically, this technique can be expressed as:

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

with $C^{\text{corrected}}$, C^{model} , and C^{obs} as the bias-adjusted, original modelled and measured concentrations at a given hour “h” and day “day”.

As stated in Monteiro et al. (2013), the global mean bias is minimised 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.

This information was added in Supplementary Material

Table S3: Add column “n” to identify number of data pairs at each site

Response: Corrected as suggested.

“Bias” appears to be the difference between the observed and modelled means. Check?

Response: Yes, “bias” is the difference between modelled and observed means, in this order and a note to clarify this was included in the Supporting Information text.

NOTE: All changes introduced in the manuscript are presented below:

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

6
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15
16 **Abstract**

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

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

7

8

1 **1 Introduction**

2 Semi-volatile organic compounds (SVOCs) are widespread chemicals that even at low
3 concentrations possess carcinogenic capacity (Baussant et al., 2001) and ecotoxicity (Solé,
4 2000) due to their persistence in different environmental matrices (air, soil, water, living
5 organisms). In particular, polycyclic aromatic hydrocarbons (PAHs) are originated by natural
6 and anthropogenic combustion processes or released from fossil fuels (Mastral and Callén,
7 2000) and can be transported in the atmosphere over long distances in gaseous phase or as
8 particulate matter (Baek et al., 1991). The lighter PAHs (2 or 3 aromatic rings) exist mainly
9 in the former, whereas the heavier (5 to 6 rings) consist almost entirely of the latter
10 (Bidleman, 1988), and this is the case of 5-ringed benzo[*a*]pyrene (BaP), arguably the most
11 studied PAH. BaP is the reference for PAH air quality standards, as defined by the European
12 Commission (Directive 2008/50/EC), which sets a limit of 1 ng m⁻³ over a 1-year averaging
13 period (European Commission, 2008).

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

24 Moreover, measurements of pollutants such as PAHs are labour-intensive compared to those
25 of criteria air contaminants such as ozone and particulate matter, and the processes governing
26 their atmospheric fate and representation within chemistry transport models (CTMs) are not
27 yet well understood (Galarneau et al., 2013), particularly in terms of uncertainties associated
28 with the emissions and re-emissions from sinks, partition patterns, volatility and fate of
29 SVOCs, among others. A number of atmospheric modelling studies have tried to characterise
30 the levels and spatial-temporal patterns of PAHs (most of them focusing on BaP) using
31 CTMs both on global (Sehili and Lammel, 2007; Lammel et al., 2009; Friedman and Selin,
32 2012) and regional scales (Matthias et al., 2009; Aulinger et al., 2011; Bieser et al., 2012;

1 San José et al., 2013). These authors identify a lack of measurement data in Europe to
2 evaluate the behaviour of the CTMs against observations. For example, Bieser et al. (2012)
3 use only six European Monitoring and Evaluation Programme (EMEP) stations (four in the
4 Scandinavian region) and six additional sites in Germany and the UK to evaluate their year
5 2000 simulations. Bernalte et al. (2012) also highlight the importance of studies on PAHs
6 over the Western Mediterranean (Iberian Peninsula) in order to increase the knowledge of the
7 ambient levels in this region. For that purpose, San José et al. (2013) conducted a 12-week
8 modelling study supported by a field campaign to describe the behaviour of their
9 WRF+CMAQ simulations, but using only a single location in Spain.

10 Hence, there is a strong need to have trustful information on the atmospheric levels of
11 compounds like BaP and other SVOCs, in particular in areas with limited information, like
12 over the Iberian Peninsula. In that sense, vegetation species can play a decisive role as
13 biomonitors of the incidence and chemical transport of atmospheric pollutants (Maddalena et
14 al., 2003). Coniferous trees are particularly important, given their worldwide distribution and
15 specific characteristics. However, even if some studies report geographical or temporal
16 patterns of PAHs in coniferous needles (Weiss et al., 2000; Hwang and Wade, 2008;
17 Lehndorff and Schwark, 2009; Augusto et al., 2010; Ratola et al., 2010; Amigo et al., 2011;
18 Ratola et al., 2012) only a few deal with their air-vegetation distribution (St-Amand et al.,
19 2009a; 2009b). In addition, to our knowledge there is no study regarding the simultaneous
20 use of field and modelling data to assess the distribution of PAHs between air and pine
21 needles. Consequently, if trustful estimates of the atmospheric incidence could be obtained
22 from vegetation, the abundance of biomonitors such as pine needles would provide essential
23 information about the regional and global atmospheric behaviour of persistent contaminants.

24 Under these premises, the WRF+CHIMERE modelling system, coupled to BaP emission data
25 from EMEP was run and evaluated for the Iberian Peninsula. The modelled depositions were
26 compared to data from biomonitoring campaigns carried out along 70 sites, to assess the
27 ability of the model to reproduce BaP canopy deposition. Monitoring data from EMEP
28 (Torseth et al., 2012) was used to validate the modelled atmospheric BaP climatologies
29 (2006-2010). A total of six approaches were tested to estimate the conversion of BaP levels
30 from vegetation into air. To achieve this, the atmospheric levels from these approaches were
31 evaluated against the modelled air concentrations.

32

1 **2 Experimental section**

2 **2.1 Pine needles sampling**

3 The Iberian Peninsula, located in the SW of Europe, has an area close to 600,000 km² and a
4 population of almost 60 million, the majority of which distributed along the Atlantic and
5 Mediterranean coastlines, except for some important conurbations such as Madrid, Seville or
6 Zaragoza. Forests (with several pine species commonly present) are scattered through the
7 whole territory. Mountainous areas follow the same trend, with the most elevated chains
8 found in the Northern borders (Pyrenees and Cantabria) and in the south (Sierra Nevada).
9 Rural activities can be found almost everywhere, but are particularly important for the
10 economy in the central plateau, where population density is scarcer. A representation of the
11 different land uses in the target domain as represented by the WRF+CHIMERE modelling
12 system can be found in Ratola and Jiménez-Guerrero (2015). ~~(but with a clear predominance~~
13 ~~in the north half) and several pine species are commonly present.~~ In this study, and
14 according to their availability, needles from *Pinus pinaster*, *Pinus pinea*, *Pinus halepensis*
15 and *Pinus nigra* with up to 1.5 years of exposure to contamination were collected from the
16 bottom and outer branches, placed in sealed plastic bags, kept from light and frozen until
17 extraction. The sampling campaigns were carried out in 33 sites in Portugal and 37 in Spain,
18 in both cases including urban, industrial and rural or remote areas. For further description of
19 these campaigns, the reader is referred to Ratola et al. (2009; 2012).

20 **2.2 Pine needles analysis and quantification**

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

25 **2.3 Methods for the estimation of BaP air concentrations from vegetation.**

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

1 parameter) were tried and the resulting estimated BaP concentrations compared with the
2 modelling experiments.

3 **Approach 1a.** This approach is based on the studies by St. Amand and co-workers (2007;
4 2009a; 2009b), who measured the levels of PBDEs and PAHs in vegetation (Norway spruce
5 needles in this case) and in the surrounding atmosphere (both gas-phase and particulate
6 material) and presented a strategy to estimate the air concentrations from those in vegetation
7 and vice-versa. In brief, the atmospheric concentration of SVOCs (C_a) estimated from the
8 levels in vegetation can be determined by the contribution of particle-bound (C_p) and
9 gaseous (C_g) phases. In the case of BaP, being a high molecular weight PAH, the gas-phase
10 contribution is negligible, which means ϕ (ratio between particle and particle+gas phases) ≈ 1
11 and C_a can be given by:

12 $C_a = C_p + C_g$ (1) with

13 $C_p = (C_{vp} * m) / (A * v_p * t)$ (2) and

14 $C_g = (C_{vg} * m) / (A * v_{gt} * t)$ (3)

15 where C_{vp} , C_{vg} - contribution of particle-bound ~~and gaseous~~ deposition processes to the
16 total concentration in vegetation, ~~respectively~~ (ng g^{-1}); m - dry weight of pine needles (g); A -
17 total surface area (m^2) of vegetation (in our study, pine needles); v_p - particle-bound
18 deposition velocity (m h^{-1}); ~~v_{gt} - net gaseous transfer velocity (m h^{-1});~~ t - environmental
19 exposure time of pine needles (h) with C_p ~~and C_g~~ expressed in ng m^{-3} . ~~In the case of BaP,~~
20 ~~being a high molecular volume PAH, the gas phase contribution is negligible, which means ϕ~~
21 ~~(ratio between particle and particle+gas phases) ≈ 1 and that v_p can be calculated directly by~~
22 ~~equation 2. However, s~~Since it was impossible to calculate v_p for our samples, due to the lack
23 of information on the atmospheric concentrations, in this first approach the value calculated
24 by St. Amand et al. (2009a) for Norway spruce (*Picea abies*) needles was used: 10.8 m h^{-1} .
25 Values of the mass and total surface area for the pine needles studied are presented in Table
26 S1. The exposure time was estimated considering that the new needles sprung out on April
27 15 and counting the hours from this day to the sampling date.

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

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

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

$$12 \ln K_v = (1000/T) * \text{slope} - 35.95 \quad (42)$$

13 with T – air temperature (K); slope – calculated by Simonich and Hites (1994) for some
 14 PAHs. And from K_v, the air concentration of PAHs (C_a) can be estimated by (in ng m⁻³):

$$15 C_a = C_v / (K_v * \text{lipid}) \quad (53)$$

16 with C_v – concentration in the vegetation (ng g⁻¹, dw); lipid – lipid content per dry weight of
 17 pine needles (mg g⁻¹, dw). Values of the lipid content for the pine needles studied are
 18 presented in Table S1.

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

21 From acenaphthylene to chrysene:

$$22 C_a = C_v / \exp [(\log K_{oa} - 7.9603) / 0.4557] = 0.4557 * \ln (C_v / C_a) + 7.9603 \quad (64)$$

23 with C_a – concentration in air (ng m⁻³, dw); C_v – concentration in the vegetation (ng/g, dw);
 24 ~~C_a – concentration in air (ng m⁻³, dw)~~

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

$$27 C_a = C_v / \exp [(\log K_{oa} - 12.18) / (-0.2272)] \log K_{oa} = -0.2272 * \ln (C_v / C_a) + 12.18 \quad (75)$$

28 ~~Log-log~~ K_{oa} is a temperature-dependent coefficient, and was calculated using the following
 29 equation:
 30

$$\log K_{oa} = A + (B/T) \quad (86)$$

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):

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

~~being $k_{max} = 0.015 \text{ s}^{-1}$ and $K_{O_3} = 2.8 \times 10^{-13} \text{ cm}^3$. 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

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

$$3 \quad F = -v_d \times C \quad (8)$$

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

9 The deposition over vegetal canopies in CHIMERE for particles employs a resistance scheme
10 (Wesely, 1989). The dry deposition velocity follows the formulation of Seinfeld and Pandis
11 (1997):

$$12 \quad v_d = (1/(r_a + r_b + r_a \times r_b \times v_s)) + v_s \quad (9)$$

13 where r_a is the aerodynamic resistance (or aerodynamic drag) and r_b the resistance at the
14 quasi-laminar sublayer. The aerodynamics resistance is calculated as the integral of the
15 inverse of the diffusivity coefficient K_z up to the middle of the model surface layer, which
16 can be estimated using the analytical formulae of the surface-layer similarity profiles for K
17 (Seinfeld and Pandis, 1997) and v_s stands for the sedimentation velocity. For vegetal
18 canopies, as in our case, corrections have been implemented. These corrections are not
19 detailed in the CHIMERE manual (<http://www.lmd.polytechnique.fr/chimere/>), but rather
20 supported on the literature presented (Giorgi, 1986; Peters and Eiden, 1992; Zhang et al.,
21 2001). For this reason, and for the sake of brevity, the same strategy is adopted here and
22 readers are referred to those works for further details.

24 **3 Results and discussion**

25 **3.1 Model evaluation for vegetation and air levels**

26 The model climatologies for BaP in canopy deposition and air concentration were done under
27 the premise of constituting a base for a broad spectrum of studies within the air-vegetation
28 interactions. In fact, a description of these simulations was mentioned previously by Ratola
29 and Jiménez-Guerrero (2015). However, given the importance for the current study, a
30 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):

$$F = v_d \times C \quad (9)$$

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):

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

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

1 (equivalent for the model and the pine needles). The results indicate an overall good ability
2 of the model to reproduce the vegetation's uptake of BaP, when compared to the
3 biomonitors. Generally, the modelled concentrations tends to be overpredicted the
4 concentrations during DJF, MAM and SON, when the deposited BaP is overestimated by
5 0.08 to 0.17 ng g⁻¹ (MFB up to +17%). On the other hand, in summer (JJA) the model is
6 likely to underpredict the measured levels in vegetation (-0.41 ng g⁻¹, -39% as MFB),
7 seemingly due to its tendency volatilise SVOCs as a result of the high temperatures simulated
8 over the Iberian Peninsula. The RMSE remains under 1.5 ng g⁻¹ in all seasons (Table 1),
9 indicating a close approach of the model to the levels obtained in pine needles. Particularly
10 noticeable is the accurate reproduction of the spatial patterns. In fact, the estimates from the
11 spatial correlation coefficient (which is highest for MAM and lowest for SON, ranging from
12 0.77 to 0.87 for all seasons) indicate that regardless of the model bias, the spatial
13 reproducibility of the deposition patterns over the Iberian Peninsula is very well reproduced
14 in all seasons, capturing also the seasonal distribution.

15 In terms of the modelled levels in canopies, Figure 1 shows that the deposition of BaP are
16 clearly lowest for JJA (under 3 ng g⁻¹ over most of the Iberian Peninsula) and have the
17 highest values in DJF and MAM (10-20 ng g⁻¹ over north-western Iberian Peninsula and the
18 Cantabria coast). But apart from the geographic distribution being closely related to the
19 emitting areas, the differences in the entrapment of PAHs by the different land uses can play
20 an equally significant role, as observed in the spatial uptake patterns shown in Figure 1. Even
21 if a discussion on the role of the different pine species is beyond the scope of this work,
22 several points were brought to our attention. For instance, it was shown previously that *P.*
23 *pinaster* needles have a superior uptake capacity towards PAHs than *P. pinea* (Ratola et al.,
24 2011) or *P. nigra* ones (Piccardo et al., 2005). The first two species have a strong
25 implantation in the forests of the Iberian Peninsula, but while *P. pinea* is more equally
26 distributed (although mainly present in the south and Mediterranean coast), *P. pinaster*
27 prevails in the north-west and Atlantic coast. This may be the reason why the model tends to
28 present higher deviations over the northernmost biomonitoring points (*P. pinaster*, MFB =
29 21%) than over eastern-southern areas, with predominant *P. pinea* (MFB = -17%), as shown
30 in Table S3 of the Supporting Information). It was also suggested that leaf surface properties
31 are more a function of the environmental exposure than of the plant response (Cape et al.,
32 1989). Given all these facts, both chemistry transport models and other parameterisations

1 face a huge task to represent the levels of pollutants in vegetation. In this sense, enhancing
2 the field experimental work on the uptake of these chemicals would be strongly beneficial.

3 **3.1.2 BaP air climatology**

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

9 Since the main focus of this work is on the climatologies of the atmospheric BaP levels, in
10 order to assess the correct reproducibility of their spatial-temporal patterns the
11 WRF+CHIMERE BaP modelled concentrations were evaluated against EMEP air quality
12 data after the bias removal—adjustment explained in the [methodology—Supporting](#)
13 [Informationsection](#).

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

25 Modelled BaP concentrations in the atmosphere (Figure 3) achieve a maximum during the
26 winter months (DJF), that can reach over 300 pg m^{-3} in most polluted areas (NW Spain and
27 western coast of Portugal), while background areas hardly exceed 5 pg m^{-3} (lowest
28 concentrations in the SE Levantine coast). The highest BaP concentrations registered
29 measured using pine needles as the biomonitoring matrix and atmospheric concentrations
30 simulated by the model were found in urban and industrial settings, mainly distributed along
31 the north-western coast of the Iberian Peninsula (as also reported by Amigo et al., 2011 and
32 Ratola et al., 2012) followed by rural and remote areas. This reflects the accumulation of

1 anthropogenic sources like traffic, building heating or industrial processes involving
2 combustions in the most populated areas of the Iberian Peninsula. Due to the characteristics
3 of such sources, a tendency to seasonality can be anticipated as well. In the colder months,
4 traffic and building heating are increased and this is not only reflected by the field
5 measurements (Ratola et al., 2010), but also by the models, as shown in Figure 3.

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

16 **3.2 Comparison of vegetation-to-air approaches**

17 Databases on the atmospheric levels of SVOCs are already available, but the existing ones
18 (like EMEP) do not cover, for instance, the entire Iberian Peninsula for a climatologically-
19 representative period of time (apart from some isolated measurements). In terms of
20 vegetation, the scenario is even worse, but since the presence of SVOCs in such
21 environmental matrices (and in particular in pine needles) reflects entirely an entrapment
22 from the atmosphere (Hwang and Wade, 2008), these measured data can be used not only to
23 validate the model results in vegetation but also to complement the information gathered by
24 the direct atmospheric sampling. For that purpose, six approaches to convert the
25 concentrations found in the 70 sites where pine needles were collected into atmospheric
26 levels were compared to the reference provided by the CTM simulations. This hypothesis is
27 based on the fact that models represent correctly the measured atmospheric concentrations of
28 BaP over the Iberian Peninsula, taking into account the evaluation against EMEP field
29 measurements available. This hypothesis was forced by the lack of simultaneous samplings
30 of vegetation and air concentrations over the target area. Therefore, we used the following
31 methodology: (a) validate simulations with WRF+CHIMERE data against EMEP network
32 measurements, in order to check the ability of the CTM to reproduce atmospheric

1 concentrations over the entire Iberian Peninsula; (b) once proven that errors are acceptable
2 and that the model shows no trend bias, use modelled atmospheric concentrations as a
3 consistent reference that allows us to compare various vegetation-to-air estimating methods
4 and check which is the most suitable approach for the particular conditions of the area.

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

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

26 Being one of the latter, BaP in pine needles may not experience the same level of seasonal
27 variation as in the atmosphere, even if it presents a similar trend. These seasonal differences
28 can be much stronger in the atmosphere, due to the fluctuation of the emission rates from
29 winter to summer. It is then not surprising that the model underestimates the atmospheric
30 concentrations of BaP measured in the colder months and overestimates them in the warmer
31 ones, since in this case the field values are obtained from the levels found in the pine needles.
32 Approach 1d is also the best representation for this seasonal variability (estimated as the
33 standard deviation between approaches and the CTM). Additionally, this approach shows the

1 best air/vegetation relationship simulated by the model, with the rest of the methods
2 providing unrealistic concentrations when compared to the measurements in EMEP stations
3 and modelling results. In fact, approaches 1a and 2 tend to underestimate the modelled
4 concentrations by a factor up to 10, yielding negative biases for all seasons. The rest of the
5 approaches greatly overestimate the levels of BaP (by a factor of 100 in the case of 1c and 3
6 and of 1000 in approach 1b). These large variations are mainly caused by the difference in
7 the deposition velocities used in each approaches 1a to 1d (from 10.8 m h⁻¹ in 1a to 0.0039 m
8 h⁻¹ in 1b) and in completely different vegetation-to-air estimation strategies in approaches 2
9 and 3. The deposition velocity has an important role in one of the three methodologies for
10 estimating air concentrations from vegetation (methodology which derives into approaches
11 1a to 1d), but it allows precisely to understand the differences that may occur when
12 conditions are changed (different species, different locations, different times of the year in
13 the same locations, different affecting sources, etc).

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

25 Finally, spatial correlation coefficients (which provide a simulation for the adequate
26 representation of the BaP spatial patterns over the Iberian Peninsula) are correctly reproduced
27 by all approaches (Table 2). The highest value is seen for winter in approach 2 (*r*=0.68) and
28 for the rest of the seasons, approaches 1a-1d present the higher correlation coefficients (from
29 0.67 in JJA to 0.85 in MAM). Approach 3 generally offers the lowest spatial correlation
30 coefficients for all seasons, except in summer. The fact that the lowest *r* values are generally
31 found for winter and summer (~~when also~~ the extremes of BaP concentrations ~~are found~~ in the
32 environment), highlights the limitations of the model to represent these extremes.

1 Ideally, the air levels SVOCs are measured in the field using expensive active air sampling
2 equipment which also require permanent power supply while operating. Thus, these devices
3 only exist in certain parts of the world, which does not allow a proper coverage of the global
4 presence of such contaminants, which naturally hinders the efforts of modelling estimation as
5 well. As mentioned above, as living structures vegetation matrices have morphological,
6 physical and chemical behaviour that depends on many parameters, even within the same
7 species. Thus, the equations describing the air-vegetation partition suffer from these effects
8 when a broad solution is searched for. Again in ideal terms, only a direct comparison of field
9 campaigns and active air sampling performed in the same spots is bound to achieve some
10 accuracy, if it includes a seasonal framework as well. In fact, the main approaches presented
11 in this work derive from these type of combined studies. But when it is impossible to have
12 simultaneous active air and biomonitoring sampling models can help us to assess if the
13 assumptions we are working with are sound, if a previous validation with the field-based air
14 concentrations is successful (as is the case in our study). Naturally, there is a concern that the
15 uncertainty associated to all the steps involved may affect the conclusions of a study like this.
16 Even if a detailed analysis would be extremely complex and out of the scope of this work, the
17 main source of uncertainty of our global process can be identified: the emission inventories
18 for PAHs, as stated by San José et al. (2013). In general, this uncertainty was estimated to be
19 within a factor of 2 to 5 (Berdowski et al., 1997), much larger than any other uncertainty
20 associated to the validation process and rest of steps. For instance, EMEP individual
21 measurements should have a precision within $\pm 10\%$ and the data quality objectives for the
22 sampling and chemical analysis set a combined uncertainty between 15 and 25% (EMEP,
23 2001). Also, the analytical methodology to quantify BaP in pine needles have similar
24 precision values (Ratola et al., 2009). The contribution of these processes to the global
25 uncertainties would be reduced in comparison to the BaP emissions.

26 =

28 **4 Conclusions**

29 This work proved the good performance of pine needles as biomonitors of the BaP
30 atmospheric concentrations. Results show that the WRF+CHIMERE modelling system
31 reproduces accurately not only the atmospheric presence of BaP, with deviations below 0.4
32 ng g^{-1} , but also the spatial and temporal patterns of its concentrations over the vegetation in

1 the Iberian Peninsula (biases lower than 30% for all stations and seasons). From the six
2 methods tested to convert vegetation levels (in pine needles) into atmospheric concentrations,
3 approach 1d showed the most accurate results, followed by approach 1a, when compared to
4 modelling results and observations from EMEP. However, these results should not be
5 interpreted as a ranking of the general performance of the approaches. For instance, given
6 that approaches 1a, 1b, 1c and 1d only differ on the deposition velocity considered for BaP,
7 we can conclude that approach 1d is the one representing more closely the particular
8 conditions of the target area. Nevertheless, for other locations and frameworks, further
9 research should be conducted to verify these conclusions. Another very important aspect to
10 take into account is that none of the studies where the available approaches were reported
11 used needles from the same pine species of the current study nor was located in areas of
12 similar climatic or geographical conditions. These facts can considerably alter the uptake
13 conditions of the pollutants, hence the different deposition rates reported.

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

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

32 The relevance of these findings open the possibility that pine needles can be used to assess
33 the temporal and spatial behaviour of BaP or other priority pollutants under completely

1 innovating perspectives. Namely allowing a reliable understanding of the air quality in areas
2 where common air sampling devices are unavailable. The comparison of levels within a
3 regional scale will enable the strong enhancement of the knowledge available so far in the
4 scientific literature for studies on atmospheric chemistry and transport of trans-boundary
5 SVOCs, which is scarce (even more if we consider model validation against experimental
6 data). Despite these promising results, further research is still needed and should be devoted
7 to: (a) study the applicability of the methods tested to different areas (both geographically
8 and in terms of land use) and (b) assess the performances of different vegetation species and
9 their ability to act as biomonitors of the atmospheric presence of several classes of hazardous
10 compounds.

11

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21

22 **Supporting information available**

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

26

27

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- 8

1 **TABLE AND FIGURE CAPTIONS**

2

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

5

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

9

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

13

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

16

17 **Figure 3.** BaP climatologies (pg m^{-3}) over the Iberian Peninsula (from top-down and left-
18 right): winter (DJF), spring (MAM), summer (JJA) and autumn (SON) for the period 2006-
19 2010.

20

21

22

1 Table 1. Seasonal evaluation of WRF+CHIMERE modelled BaP depositions results (over
 2 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±<u>STD DEV</u> (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

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

7

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

	DJF	MAM	JJA	SON
CTM MEAN* <u>±STD DEV</u> (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 <u>±STD DEV</u> (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 <u>±STD DEV</u> (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 <u>±STD DEV</u> (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 <u>±STD DEV</u> (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 <u>±STD DEV</u> (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 <u>±STD DEV</u> (pg m ⁻³)	1299.80±342.94	1230.83±333.38	974.41±36.72	998.15±41.59

4 *Modelling results are considered as a consistent reference to compare the estimations from the different
 5 approaches. DJF – December, January and February; MAM – March, April and May; JJA – June, July and
 6 August; SON – September, October and November; CTM – chemistry transport model concentrations; STD
 7 DEV – standard deviation; CORR- COEF- – correlation coefficient; MFB - mean fractional bias; RMSE - root
 8 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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24

25 Pine needles analysis and quantification

26

27 Duplicate samples of 5 g of needles underwent ultrasonic extraction (USE) with a mixture of
28 hexane:dichloromethane (1:1) as solvent and were subsequently cleaned-up using 5g alumina
29 solid-phase extraction (SPE) cartridges from International Sorbent Technology (Mid
30 Glamorgan, UK), using the same solvent for elution. After blowing down to dryness and
31 solvent change to hexane, chromatographic analysis of BaP was done in a Varian CP-3800
32 gas chromatograph (Lake Forest, CA, USA) coupled to a Varian 4000 mass spectrometer in
33 Portugal and a Trace GC 2000 Series gas chromatograph from TermoQuest (Waltham, MA,
34 USA) coupled to a Finnigan Trace MS 2000 Series mass spectrometer in Spain. However,
35 the operation was similar in both cases, namely using electron impact ionization (70 eV), a
36 J&W Scientific (Folsom, CA, USA) 30 m × 0.25 mm I.D. DB-5 column coated with 5%
37 diphenylpolydimethylsiloxane (film thickness 0.25 µm) and the same oven temperature
38 program. The injector, transfer line and ion source temperatures were also the same (280, 250
39 and 200 °C, respectively). Finally, the acquisition was made in single ion monitoring (SIM)
40 mode using deuterated PAHs as surrogate standards. BaP was identified and quantified using
41 retention time and up to three ions, with perylene-d₁₂ acting as surrogate standard and
42 anthracene-d₁₀ as internal standard to look for GC-MS errors.

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

48

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

	<i>P. pinea</i>	<i>P. pinaster</i>	<i>P. halepensis</i>	<i>P. nigra</i>
Mean mass of one needle (g)^a	0.06	0.13	0.018	0.035
Mean surface area (m²×10⁻⁶)^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

50 ^a Data taken from Daligault (1991) and Moro (2006)

51

52 **Modelling experiment**

53

54 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	

55

56 The Advanced Research Weather Research and Forecasting (WRF-ARW) Model v3.1.1
 57 (Klemp et al., 2007; Skamarock et al., 2008) is used to provide the meteorology to the
 58 chemistry transport models. WRF is a fully compressible, Eulerian non-hydrostatic model
 59 that solves the equations that govern the atmospheric motions. 33 vertical layers on sigma
 60 coordinates cover from the ground level up to 10 hPa. Microphysical processes are treated
 61 using the single-moment 3-class scheme described in Hong et al. (2004). The sub-grid-scale
 62 effects of convective and shallow clouds are resolved by a modified version of the Kain-
 63 Fritsch scheme based on Kain and Fritsch (1993). The Noah land surface model was used to
 64 solve the soil processes on 4 layers to a depth of 2m (Chen and Dudhia, 2001a; 2001b). The
 65 vertical sub-grid-scale fluxes caused by eddy transport in the atmospheric column are
 66 resolved by the Yonsei University non-local planetary boundary layer scheme (Noh et al.,
 67 2003). Finally, radiation was treated through the Community Atmospheric Model (CAM) 3.0
 68 radiation scheme (Collins et al., 2006).

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

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

$$85 \quad J_i = 1 / \tau_i (G_i - G_{i\text{eq}})$$

86 Where J_i ($\mu\text{g m}^{-3} \text{s}^{-1}$) is the absorption or desorption flux of species i ; τ_i (s) is a characteristic
87 time of the mass transfer that is a function of particle size and the chemical properties of i ; G_i
88 is the bulk gas-phase concentration of i and $G_{i\text{eq}}$ is the gas-phase concentration of i at
89 equilibrium. The gas-phase concentrations at equilibrium depend on the chemical
90 composition of the particles, the temperature and, for hydrophilic species, the relative
91 humidity (Pun et al., 2006).

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

104 Anthropogenic emissions for the entire period of simulations are derived from the EMEP
105 database (Vestreng et al., 2009) and disaggregated to the working resolution following spatial
106 proxy data, according to the methodology stated in Pay et al. (2010). For BaP emissions, data

107 have been obtained from the EMEP-MSCEAST web site (<http://www.msceast.org>). The
108 accuracy of simulations depends strongly on emission data and unfortunately there are strong
109 uncertainties in BaP emissions, by a factor of 2 to 5 (San José et al., 2013). According to
110 these authors, the main source of BaP is incomplete combustion processes of organic
111 material, in particular wood and coal in private households. Industrial heating and cookeries
112 as well as road traffic are also large sources of BaP, which is emitted in particle phase.

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

120

121 **Model validation**

122

123 EMEP stations are located at a minimum distance of approximately 10 km from large
124 emission sources and thus assumed to fit the resolution of the model used for regional
125 background concentrations (Torseth et al., 2012). Thus, as reported by Ratola and Jiménez-
126 Guerrero (2015), results from the EMEP monitoring data were used to characterize the ability
127 of the model to reproduce present air BaP levels and variability. The “EMEP Manual for
128 Sampling and Analysis” (EMEP, 2001) describes all the sampling methodologies employed
129 for each chemical and/or matrix and the recommended operation, as well as the data quality
130 objectives for the yielded results. Regarding the uncertainty, no information is given for the
131 Iberian sites, but it should meet the EMEP data quality objectives for the combined sampling
132 and chemical analysis (between 15 and 25%). This fulfillment (among others) leads to the
133 validity of the results presented. Final

134 in the 2006-2010 time frame were: Niembro (2006-2010), Campisabalos (2007-2008), O
135 Saviñao (2007), Víznar (2008-2010), Peñausende (2008-2009), Barcarrota (2008), Zarra
136 (2008), San Pablo de los Montes (2009-2010), Mahón (2010) and Els Torms (2010). In all of
137 them, BaP ~~measurements are available as weekly or monthly averages~~frequencies of
138 measurement and duration varied probably depending on the budget limitations, but when

139 sampling campaigns were active, they were performed usually once a week.- The results
140 (available as weekly or monthly averages) have been~~were~~ compared to the available periods
141 for observations.-The handling of samples is taken with extreme care to limit external
142 contaminations and/or degradation reactions to occur. For the more volatile chemicals, there
143 is a bigger risk of having some losses, but in the case of BaP, since it is almost all formed by
144 particulate matter, it is bound to stay stable under the appropriate storage conditions
145 (commonly in the freezer until analysis). The results (available as weekly or monthly
146 averages) were compared to the available periods for observations. Regarding the
147 uncertainty, no information is given for the Iberian sites, but it generally should meet the
148 EMEP data quality objectives for the combined sampling and chemical analysis (between 15
149 and 25%) (EMEP, 2001).

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

159
160 For the evaluation of canopy deposition and atmospheric concentrations, a number of
161 statistical parameters have been selected (Figure S1). Spatial correlation coefficient (r), root
162 mean square error (RMSE) and mean bias (MB) values are commonly used by the modelling
163 community and have therefore been selected according to the criteria of Pay et al. (2010),
164 who use them to evaluate a modelling system for Europe (-“bias” is intended as the
165 difference between modelled and observed means). Moreover, Boylan and Russell (2006)
166 suggest that the mean normalised bias error (MNBE) for each model-observed pair by the
167 observation is a useful parameter, but may not be appropriate for evaluating particulate
168 matter and their components. These authors suggested the mean fractional bias (MFB) and
169 the mean fractional error (MFE) instead, indicating that model performance goal would be
170 met when both the MFE and MFB are less than or equal to 50% and $\pm 30\%$, respectively, and
171 the model performance criterion when $MFE \leq 75\%$ and $MFB \leq \pm 60\%$. These criteria and

172 goals have been selected to provide the metrics for the WRF+EMEP+CHIMERE evaluation
 173 of BaP. Annual and seasonal mean statistics are computed, with seasons corresponding to
 174 December, January and February (DJF, winter), March, April and May (MAM, spring), June,
 175 July and August (JJA, summer) and September, October and November (SON, autumn).

176

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

177

178 Figure S1. Main statistical parameters used in model validation

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

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

195
196 Figure S2. Mathematical expression for the bias-adjustment of the modelled results.

197 As stated in Monteiro et al. (2013), the global mean bias is minimised the for all the
198 monitoring stations, using the bias detected in previous days for a given hour (h) of the day.

199 These procedures are model, site, and time of day specific.
200

201 **Results**

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

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

205 Table S3. (cont.) Parameters of the modelled deposition over vegetal canopies evaluated
 206 against observations compiled from pine needles, for all the sampling points (n – number of
 207 duplicate samples; mean concentrations in ng g⁻¹).
 208

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

209

210

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