Atmospheric
Chemistry
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Discussions

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

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IMPORTANT: All changes introduced in the manuscript are presented in a pdf file uploaded in "Supplement (pdf/zip)"

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 unintentionally 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 x 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 = kmax [O3]/(1 + KO3[O3]) (eq. 7)

being kmax= 0.015 s-1 and KO3 = 2.8 x 10-13 cm3"

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.âĂĺ 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 adsportion, benzo[a]pyrene degradation, and atmospheric implications. J. Phys. Chem. A 2001, 105, 4029-4041.âĂĺ

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 Ca = xxx

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

Why was a three-month average temperature used for Koa 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 Koa (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 Koa 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 pro-

cess 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 fur Umwelt, Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungbericht 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): $J_i = 1/\tau_i (G_i - G_{ieq})$

Where J_i (μg m-3 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_{ieq} 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).âĂĺ

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?

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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:

(see Figure S2)

with Ccorrected, Cmodel, and Cobs 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 the for all the monitoring stations, using the bias detected in previous days for a given hour (h) of the day. These procedures are model, site, and time of day specific. 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.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C12941/2016/acpd-15-C12941-2016-supplement.pdf

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

Fig. 1. Figure S2. Mathematical expression for the bias-adjustment of the modelled results

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