

## ***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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Received and published: 2 March 2016

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 #2

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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

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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.

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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 biomonitoring (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

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and conclusions.

Response: This is indeed a very important and pertinent point, as the use of biomonitoring 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 biomonitoring 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 biomonitoring 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 biomonitoring 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

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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

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for english phrasing: e.g. p26497 I13: "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.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C12934/2016/acpd-15-C12934-2016-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 26481, 2015.