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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories" *by* M. S. Alam et al.

Anonymous Referee #1

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Overall Comment and Recommendation:

This manuscript examines the potential use of congener profiles of parent PAHs and quinones, together with back-air mass trajectories to support the emission source areas for these toxic compounds in a rural site in eastern England. The sampling campaigns of approximately one month in summer and winter allow the study of an extensive data set. Although the results of the chemical analysis prove the usefulness of the isomeric ratio analysis for parent PAH and quinones, the discussion based on the

origin of the sampled air masses is weak, many times due to lack of significance in the correlations. Maybe this was caused by the simplified method to cluster trajectories into the three cluster, although the variance of the origin (i.e. trajectory) may not be that clear. Since the authors used an on-line version of the hysplit model, recalculation of the one of the most important days of the sampling in winter (11-14 February) shows that these trajectories are passing Scandinavia, while they are coded in the manuscript as North Atlantic trajectories. Therefore the used clusters may be misfortunate and the whole discussion and conclusions wrong. Since this issue is one of the main points in this manuscript, the authors need to demonstrate if they are sure of their findings and if the difference between 'origin' (or trajectory) are significant or not. If there no significance (i.e. difference), then they should discuss this.

Specific comments:

Abstract.Page 25742.Line 4. The sampling periods in the urban and rural site are not in the same period. This may create already difference between concentrations. It is better to leave this comparison to the discussion of the results, instead of stating this in one of the first sentences of the abstract. The sampling site in the present study is the rural site, and not the urban site. It creates confusion.

Page 25742. Line 5. The concentrations of the "air masses originating from Southern England" are statistically higher than the ones from "Scandinavia and the North Atlantic"?

2.2. Particle and vapour sampling. Page 25745. Line 9. Is there any degrading effect observed on the PUFs by using dichloromethane as extraction solvent?

2.4. Back trajectories. Page 25747. Line 1. It is not clear to the reader whether the authors used the "vertical velocity", "isobaric" or "isentropic" type of trajectories. Which one was used and why. Normally there are little differences between the outcomes, but sometimes there are differences that can lead to different interpretations of the origin of the air mass.

3.1. PAH concentrations. Page 25747. The comparison between the urban site in England with the rural site in the present study could be introduced here.

Page 25748. Line 10. “The seasonal differences. . .is not explicable purely by greater partitioning to vapour in the warmer summer campaign, although this will be a factor”. What is the contribution of this factor on the partitioning of the different PAH congeners between the phases?

3.3. Back trajectories. Page 25751. Line 5. Are the authors sure about the classification of the air mass trajectories in Table S1? For example, if one recalculates the 72h trajectories for the sampling site on 11 Feb. 00.00UTC or 12.00UTC and do so for 12 and 13 Feb. . .uing “vertical velocity”, then the 10, 100 and most of the 500m trajectories pass over Scandinavia, and not the “remote North Atlantic” (see supplement). Could there be another reason for this low PAH concentrations in these days?

Page 25751. Line 11. In order to support the similarities between SO2 and PAH concentrations, the regression coefficient should be given and state whether this relationship is significant.

Page 25751. Line 15. Are the authors really sure about the origin of the air mass from the “remote North Sea” in the period between 11-14 Feb. (see comment Page 25751. Line 5). And are the differences in PAH concentrations between the “origins” of the air masses significantly different. If not, why not? Could the methodology to cluster the trajectories have something to do with this? This should be clarified.

In the part on the back trajectories (3.3) the discussion of the summer samples is missing.

3.4 Ratios. . . Page 25752. Line 17. “A paired t-test revealed. . .campaigns” It is not clear here between which clusters there were differences. But again, are the clusters well formed?

Page 25754. The comparison between summer and winter data based on Figure 2

is confusing since “winter-green” and “summer-red” cluster are very similar. . .both in ratios as well as in trajectories.

What are the differences between “summer and winter red” trajectories (figure2)? The fact that summer-red trajectories pass over land has an influence on the chemical composition?

3.5. PAH reactivity. Page 25755.Line 27 to Page 25756.Line 4. How does the isomeric ratio between flu and pyr relate to the trajectory clusters?

Page 25756. Line 18. Can the trajectories of Birmingham be compared to the ones in the present study? There is more than 200 km distance between the sites. In the figure 4 there is a general cluster presented. How applicable is this cluster for Birmingham? What about the influence of local sources in the case of Birmingham?

Overall, the authors should revise the trajectory clustering and adapt the discussion on this revision. The chemical analyses are well presented and the discussion around the differences between possibly aged products and fresh inputs is powerful. Maybe the applicability of the trajectories is limited for its uncertainties, which is basically the large scale (1 degree. . .120km) of this model.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C9063/2013/acpd-13-C9063-2013-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25741, 2013.