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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.

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RESPONSE TO REVIEWERS: Atmos. Chem. Phys. Discuss., 13, 25741, 2013 Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories" by M. S. Alam et al.

Anonymous Referee #1 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 approx-

imately 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. RESPONSE: We thank the referee for his/her comments and have made the following necessary changes to the manuscript. We agree that the approach to clustering the back trajectories to three clusters for the entire winter campaign may be over-simplified and thus create some confusion in the assignment of each day of the campaign to a cluster. Therefore we have amended the manuscript to present the six cluster solution, and subsequently group two clusters together as discussed in detail below. We have edited the text, discussions and conclusion accordingly.

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. RESPONSE: We have amended the sentence as outlined in the manuscript to avoid confusion as the reviewer points out:

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"Concentrations of individual PAH are relatively smaller than average concentrations measured previously at urban sites in the UK."

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"? RESPONSE: Sentence has been amended as recommended. "The concentrations of PAH of the air masses originating from southern England are significantly larger than those from Scandinavia and the North Atlantic, while quinone to parent PAH ratios show an inverse behaviour, being highest in the more aged North Atlantic polar air masses."

A similar statement has been added to the main body of the text, including the test and significance level (t-test $p<0.10$)

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? RESPONSE: We have not noted any degradation of PUF substrate when using dichloromethane as extraction solvent. Sampling procedures, recoveries and uncertainties have all been rigorously dealt with in Delgado-Saborit et al., Atmospheric Environment 77, 974-982, 2013a which has been referenced. An explanation of this has been added into the manuscript.

Line 10. "where no degradation effect was observed." 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. RESPONSE: As suggested by NOAA, the default is to use the "vertical velocity" field which is included with most meteorological data and is the case here.

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. RESPONSE:

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Added here as recommended. Line 11: “Concentrations of individual PAH are 20-140 times smaller than average concentrations at an English urban site.”

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? RESPONSE: Its is difficult to estimate the contribution of greater gas phase partitioning of the different PAH congeners without knowing the contributions of the other factors, as outlined in lines 11-15. What we can say is that this would be a contributing factor along with the other factors outlined in lines 11-15. The main influence of this factor is greater reactivity in the vapour phase, which we are examining in a later paper.

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? RESPONSE: The simplified approach of the classifications of the back trajectories has been amended to a better representation, as outlined in the manuscript Page 25750-25751 (Back trajectories).

The winter trajectories could be represented by either a 3 or 6 cluster solution. We have amended the manuscript to the 6 cluster representation, but have grouped each of these clusters together according to geographical origin i.e. air masses originating from the North sea and Scandinavia were combined (red), Eastern and Southern Europe were combined (green) and London and mainland UK were combined (blue). All subsequent figures have been changed to include the revised embedded image of the 6 cluster solution.

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Other reasons for the low concentrations measured on these days maybe due to the differing temperatures of the air mass origins or of sampling. During the summer the concentration of PAH were on average 70% lower, owing to many factors including partitioning due to temperature, as discussed on Page 25748, lines 10-15. The temperatures during these specific days were the highest during the month, but this should not affect the concentrations much as the variation in temperature within the winter and summer campaigns was very small (2.9 $\pm$ 1.8 °C and 16.0 $\pm$ 2.7 °C, respectively).

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. RESPONSE: Regression coefficient has been added to the text (line 13). "(r2 Âň= 0.65)"

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. RESPONSE: This point is addressed through the new 6-cluster solution. SO2 comparison is not made here similar to that of the winter data owing to lack of SO2 measurements; therefore a small summer discussion is added here (as advised) which is expanded in much greater detail when discussing ratios in Section 3.4.

"Similarly, during the summer, lower PAH concentrations were measured during sampling periods 13 August 2010 to 16 August 2010 and 30 August 2010 to 02 September 2010, when air masses originated from the North Sea, see Figure S1B."

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? RESPONSE: The ratios calculated from samples originating

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from one cluster were different to ratios of samples originating from another; i.e. for the winter campaign the ratios determined from any pair of trajectories (North Sea and Scandinavia, Eastern and Southern Europe and London and Mainland UK), were all statistically different from one another ($p < 0.05$). The manuscript has been left as is as we believe that this is clear.

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? RESPONSE: Each embedded Figure of the trajectories within the Figures 2A and 2B explain the colour codes as outlined in the legend of the Figure. The "winter-green" cluster in Figure 2A is from Eastern Europe (now is Eastern and Southern Europe), while the "summer-red" cluster is from mainland UK and the Atlantic; therefore these are not similar as suggested by the referee.

The summer red cluster originates from mainland UK and the Atlantic, whereas winter red cluster originates from the North Sea and Scandinavia. The summer red trajectory passes over mainland UK and therefore shows enhanced levels of PAH and lower Q:P ratios, in comparison to the summer green cluster which demonstrates lower concentrations of PAH and enhanced Q:P ratios as this cluster originates from a remote origin, as illustrated in Figure 2B. The manuscript has been left as is as this is explained in the Figure and text.

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? RESPONSE: The FLU/PYR ratio for the urban site was 0.78, whereas in the rural site it was an average of 2.06, as stated on page 25755, line 24. The isomeric ratios between FLU and PYR for the trajectories are included in the manuscript on page 25756, line 4-7.

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"This is however, in contrast with the isomeric ratio of FLU/PYR for the individual trajectories calculated during the winter which are 2.06, 2.15 and 1.01 for London and mainland UK (blue), Eastern and Southern Europe (green) and North Sea and Scandinavia (red), respectively, which may suggest different ratios in the different source areas"

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 RESPONSE: The trajectories of Birmingham cannot be compared to the ones in the present study as there are various local sources of PAH in Birmingham, and therefore air mass trajectories cannot be accurately applied to source area attribution in urban locations as has been done for this study in Weybourne (a rural site).

Anonymous Referee #2 The manuscript describes the measurements of PAHs and quinones concentrations in the air samples (gaseous and particle phases) collected in remote area. The problem of quinones presence in the atmospheric air is not well described yet. In this paper, the authors for the first time report the results of atmospheric quinones determination at remote areas. The manuscript is elegantly prepared. The analytical work is well described and referred. The results are clearly presented and logic. The great value is in the searching for information about reactivity with radicals and partitioning of PAHs between the phases of parent PAHs and quinones. The other

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important point is the differences in seasonal concentrations of quinones, what gives clues about their environmental fate. I believe that the manuscript greatly contributes to understanding of atmospheric chemistry of PAHs and PAH related compounds and in my opinion can be published as it is. RESPONSE: We thank the reviewer for these thoughtful and generous comments.

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