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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of elevated wintertime PAHs by compound-specific radiocarbon analysis" *by* R. J. Sheesley et al.

R. J. Sheesley et al.

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We would like to thank the referees for their helpful comments and address each one individually. Overall the referees noted the uniqueness of the compound specific radiocarbon analysis (CSRA) for atmospheric aerosols, which was the major advance in this study. Referee 1 states "the measurements are so unique (to my knowledge, 14C analyses of individual PAHs have not yet been performed on ambient particulate matter filters) that publication of the study is justified", while Referee 2 states that "the article is very well written and the application of CSRA techniques brings some novelty." Both reviewers also provide a number of suggestions for improvements. For instance, Referee 1 requested a table of previous compound class specific results for atmospheric PAHs and a more selective discussion of the possible sources of molecular weight 276 PAHs with regards in particular to gasoline vs diesel vehicles. Referee 2 had concerns

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about sampling artifacts. We have thoroughly revised the manuscript to address these issues. We detail our responses and resulting edits below with referee comments numbered and author response number AR1, etc and additions to the text in quotes.

Referee 1: 1. P20902L18-19: This sentence is misleading, as one may understand that this fraction has a contribution of biomass combustion of 9%. It should be clarified like: "9% lower contribution of biomass combustion than the sum of all PAHs".

AR1. This sentence and the preceding have been edited for clarity to read as follows: "A simple isotopic mass balance model was applied to estimate the fraction biomass (fbiomass) contribution, which was constrained to 71-87% for the individual PAHs. Indeno[cd]pyrene plus benzo[ghi]perylene had an fbiomass of 71%, while fluoranthene and phenanthrene (gas phase) were at 87%."

2. P20902L21-23: This sentence should be removed as it does not contain any clear message.

AR2.The authors agree that the sentence as written did not function well as a concluding sentence for the abstract. The sentence has been altered to read “This CSRA data of atmospheric PAHs established that RWC is the dominating source of atmospheric PAHs to this region of the boreal zone with some variations among RWC contributions to specific PAHs."

3. P20907L28-P20908L3: The authors should also present results of the blank contribution (carbon mass and isotopic value) for the PCGC procedure. It is clear that 40 injections per extract introduce contamination into the sample. Only if these numbers are given, one can evaluate whether this contribution is significant.

AR3. In the current state of CSRA applications (in many fields of geo and environmental science), a CSRA blank of the pcGC step is not feasible because of detection limits. The mass of the individual compounds is quite low as a starting point and any potential contamination is a very small fraction of that making the radiocarbon analysis of the

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blank very difficult for pcGC. As stated in the text the purity of the individual compounds was 92-100% with an average of 97%, which means very low potential contamination. The following sentence and reference have been added to the methods "Previous studies in Gustafsson's laboratory at Stockholm University have shown limited fossil and no modern carbon contamination during the pcGC method (including potential column bleed and general sample handling), with processed and unprocessed standards showing no significant difference when the uncertainty of the AMS is considered (Zencak et al., 2007). However, TOC blanks were included in analysis. These comprised roughly 1-3% of the sample TOC. TOC radiocarbon results were blank corrected with a 0.3-1.2% change in the fM."

4. P20908L15-17, P20912L25: Substitute "error" with "uncertainty"

AR4. Done

5. P20909L24-27, Figure S1: Several studies are cited, which use CMB modeling to estimate the contribution of biomass burning. As the dataset of this work includes concentration determinations of different PAHs, the authors should provide such a CMB modeling estimation from their data (e.g. by using the PAH/OC ratios of Figure S1 or by following the concept of Schauer and coworkers) as an alternative approach in order to compare it with the 14C results.

AR5. Organic molecular marker CMB modeling as used by Schauer (and Sheesley in previous works) requires a larger set of more specific markers including hopanes, alkanes, levoglucosan and elemental carbon. Because this study was focused on apportionment of PAHs and total organic carbon using an isotopic mass balance model, the larger set of molecular markers are not available for modeling. The radiocarbon is sufficient to apportion the PAHs and TOC to biomass burning and fossil sources. The only way to split the fossil contribution, with the current data set, is an estimate of contributions based on PAH/OC ratios.

There are several comments concerning the gasoline/diesel exhaust split for the fossil

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component in Lycksele (comments 5,12, 13, 15). Basically, the concern is that Figure S1 is not conclusive evidence to determine the contribution of gasoline vs diesel exhaust in Lycksele. In order to support this hypothesis and to more fully address the comments, PAH/OC ratios from published gasoline and diesel emissions analysis (Riddle et al., 2007;Lough et al., 2007;Rogge et al., 1993)were used to calculate OC contributions based on the indeno[cd]pyrene + benzo[ghi]perylene ambient concentrations. Table S3 and a short discussion were added to the Supplemental Materials to address this question. Statements in the text regarding the gasoline/diesel split in Lycksele were also weakened to reflect the lack of conclusive information.

The following text was added to supplemental materials: "PAH/OC ratios from published gasoline and diesel emissions analysis (Riddle et al., 2007;Lough et al., 2007;Rogge et al., 1993) were used to calculate OC contributions based on the indeno[cd]pyrene + benzo[ghi]perylene ambient concentrations (Table S3). These calculations illustrate two key points: PAH/OC ratios are quite variable and dependent upon vehicle conditions and the two gasoline references are the only ones which come close to the Fossil TOC contribution as estimated by isotopic mass balance modeling. It should be noted that the ratios give an estimate of ambient OC not TOC, so these values would be expected to be biased low not high. Vehicle registration for Lycksele kommun, which includes both the city and surrounding area, indicates 86% gasoline 14% diesel (Granlund, H. and Fjällstedt, K., personal communication, 2009). These values give an indication of relative importance but still require input of source profiles in order to scale from number of vehicles to potential emission impacts. The combination of additional emission ratios for PAHs and vehicle registration numbers gives greater credence to the assertion that gasoline vehicle exhaust is dominant for fossil carbon in Lycksele, but does not prove that gasoline is the sole source of fossil PAH in Lycksele."

In addition, the lines in question from comment 13 (P20913L20-P20914L2) have been altered to read: "Figure S1 illustrates that the PAH/OC ratio for benzo[ghi]perylene, in

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particular, is much higher for the two gasoline-powered motor vehicle exhaust average profiles (Lough et al., 2007; Rogge et al., 1993) in comparison to the same ratio for wood smoke emission profiles (Lee et al., 2005; Schauer et al., 2001; Fine et al., 2002, 2004) and reported diesel-powered motor vehicle exhaust (Rogge et al., 1993; Lough et al., 2007; Riddle et al., 2007). A further exploration of the apportionment of OC based on published PAH/OC ratios for motor vehicle exhaust is included in the Supplementary Material. The results of this back calculation of ambient fossil OC from ambient fossil indeno[cd]pyrene plus benzo[ghi]perylene concentrations indicate that the published gasoline motor vehicle profiles are a better fit for this Lycksele dataset. Vehicle registration for Lycksele kommun, which includes both the city and surrounding area, indicates 86% gasoline and 14% diesel (Granlund, H. and Fjällstedt, K., personal communication, 2009). These fleet values also cannot conclusively predict the gasoline/diesel split for PAHs but combined with the available emission profile data and CSRA results gives an indication of the potential importance of gasoline motor vehicle exhaust for Lycksele PAHs."

6. P20911L15: Remove the word "then".

AR6 Done

7. P20911L21: The reference value for Delta14Cfossil should be repeated here as well. S10906

AR7 Done.

8. P20912: I recommend compiling all data in a table (considering SRM1649a, Kumata et al. (2006), all papers of Reddy et al., all papers of Mandelakis et al., etc.). It is important to note that the older data of SRM1649a (e.g. in Currie et al., 1999) were biased by an erroneous blank correction so that results of Currie et al., J. Res. Natl. Inst. Stand. Technol. 107, 279-298, 2002 should be used. The compilation will help to distinguish CSRA from CCSRA results and to show the broad range of 14C data for the PAHs. Especially, the totally different levels for SRM1649a (95% fossil) and samples at

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Lycksele (20% fossil) should be addressed.

AR8. The authors agree that this section would be much improved with the addition of a table so Table 3, which includes CSRA and CCSRA for atmospheric samples, standard reference material and fire place soot, has been added to the manuscript. Additionally, the first paragraph of P20912 has been rewritten for clarity and to reflect the inclusion of the table.

"The fbiomass ranges from 71-87% for all PAHs and the average for TOC is 77ś3%. Hence, TOC is in the middle of the fbiomass range for the measured PAHs. Several previous studies have reported the fbiomass for pooled, compound-class specific radiocarbon analysis (CCSRA) of PAHs and CSRA of household soot and NIST SRM 1649a (see Table 3). The SRM and soot were both solid/dust samples while the remaining represent filter-based samples. The Croatian and Greek values represent summer conditions whereas the Southern Sweden fbiomass (50%) is a multi-year average; a winter event at the same Southern Sweden site had an fbiomass for TOC of 75-85% (Zencak et al., 2007a), and the difference between the PAH annual average and the winter TOC illustrates the impact of seasonal sources such as RWC. Table 3 also illustrates the differences among RWC contribution across Europe. In a study in Tokyo, particulate CCSRA-PAHs in the PM10 fraction were split into low and high molecular weight fractions with little seasonal differences. Road traffic emissions might be expected to dominate in and around a megacity like Tokyo, and therefore it is surprising to see the high fraction of PAH from biomass combustion in both summer and winter. The fbiomass calculated for Lycksele is much higher than all three of these previously reported CCSRA-PAH studies and the CSRA from NIST SRM 1649a (urban dust from Washington, D.C., USA), but roughly the same as the winter TOC from southern Sweden. The fbiomass of PAHs from this study plus the fbiomass of TOC from Southern Sweden (Zencak et al., 2007a) indicate the dominance of RWC during winter in the boreal zone and the importance of not extrapolating among seasons and regions."

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9. P20912L11: Does "35-65%" refer to TOC or PAH?

AR9. The 35-65% refers to PAHs. The sentence has been edited to read A more comprehensive study of CCSRA PAHs in the western Balkans measured..."

10. P20912L15: The reference of the word "respectively" is unclear.

AR10. The first paragraph of P20912 has been rewritten to reflect the inclusion of Table 3, as detailed under comment 8.

11. P20912L22: The sentence should begin like this: "To evaluate the isotopic..."

AR11. Done

12. P20913L20-25, Figure S1, P20902L16-18: I assume that there are more studies on PAH/OC ratios of diesel and gasoline exhaust emissions than Lough et al. (2007). Results of other publications should be included in Figure S1, which should be considered in the CMB estimations and in the diesel vs. gasoline discussion. It is a weak point that Lough et al. (2007) do not present results for B[ghi]P, as I can achieve from Figure S1. As this PAH is analyzed together with I[cd]P, any interpretation of the 14C data of this PAH combination is only valid, if emission ratios for both PAHs can be found. Due to this, the corresponding clause in the abstract ("known to be enhanced in gasoline-powered motor vehicle exhaust compared to diesel exhaust") should be removed, unless better data are presented.

AR12. This comment has been addressed in the response to comment 5. The B[ghi]P in the Lough et al diesel was in the break in the graph and has now been made visual in Figure S1. The clause in the abstract has been removed.

13. P20913L26-P20914L2: This sentence should be removed as it contains too much speculation for the given 14C results of this study. To me, car fleet numbers will provide more reliable and statistically significant results then the PAH/OC ratios in combination with the 14C values of the B[ghi]P+I[cd]P combination.

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AR13. This comment has also been addressed in the response to comment 5.

14. P20914L21-23: The power of this statement contradicts the interpretation of the S10907 data in P20913L7-8 ("...inhibits statistical analysis"). The sentence should be weakened.

AR14. This sentence has been altered to read "Any decrease in RWC may have a larger impact on the lower molecular weight PAHs, as these appear to have a higher fbiomass, based on the limited results in the current study."

15. P20915L5: The power of this statement contradicts the interpretation of the data as already discussed in items 12 and 13. The sentence should be weakened.

AR15. The sentence has been weakened to read "For Lycksele, enhanced contribution of fossil fuel for the MW 276 PAHs as determined from using CSRA instead of CCSRA coupled with emission profiles and fleet numbers suggests that gasoline-powered motor vehicle exhaust may contribute more to fossil PAHs in Lycksele than diesel exhaust."

16. P20915L8-11: New discussion threads as well as literature citations are not acceptable in the Conclusions.

AR16. Agreed, this sentenced has been removed.

17. Table 1 and section 2.4: Considering all the numbers given in the manuscript, I estimate that 30 ugC were used for the 14C analyses of the individual PAHs. If this is true, it is disappointing due to the fact that there are several AMS laboratories in the world performing 14C measurements for samples $<$10 ugC on routine basis. This means that measurements could have been performed on the fortnight filters! Sample masses should be given in Table 1 or in the supplementary material.

AR17. The estimated μg C for each compound and compound pair have been added to Table S1. As can be seen from this, there is a rather wide range of masses (22-196 ug C), which means that in order to do 6 different compounds for the roughly equal periods of time, it was necessary to composite the bi-weekly samples. Although some

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labs may only require $<$10 μg of C, it has been our experience that the laboratory at NOSAMS requests at least 25-30 μg of C.

18. Table 2: New data from the study should be marked more clearly, e.g. by "this work". AR18. Done.

Refereee 2 I read the article by Sheesley et al with interest, which assess the relative impact of residential wood combustions and traffic emissions using radio carbon analysis and compound specific radiocarbon analysis (CSRA) of the samples collected from a town in Sweden. However, the article is written very well and the application of CSRA techniques brings some novelty and but I have following reservations. 1.] What is the total number of sample? Based on the description it seems that only 6 filter (after mixing only 3) and 4 PUF samples were analysed. In general, this sample number is too small for any concrete scientific conclusions and for statistical analysis.

AR1. It is true that 6 samples is not a lot, and the authors would like to address this concern. The key is that these samples should not be considered short-term "snapshots", rather these are long-term averages. The sample composites cover half of the winter 2006 season in Lycksele and should therefore be sufficient to describe that season. To address this concern in the text, the authors have included the following statement in the methods section "The samples have been composited to achieve a representative winter sample for Lycksele." The authors agree that this number is too small for statistical analysis.

2.] Sampling period for filter is two weeks, which is exceptionally more than normal. Even a similar study by Kumata et al (EST, 40, 3424, 2006) used maximum of 7 days sample, which they also claim as unusual. Further they had in total 79 samples. As highlighted by Ravindra et al (AE, 42, 2895, 2008) and reference therein that unusual long sampling period may introduce both positive and negative sampling artefacts.

AR2. The sampling periods employed in this study were long compared the common daily sampling. The reasoning for the long sampling periods was to minimize

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the impact of filter contamination by minimizing the number/area of filter composited to achieve the high masses required in radiocarbon analysis. Radiocarbon analysis is an intrinsic property, so although concentrations may be affected by sampling artifacts, the 14C/12C ratio should remain consistent. The authors intended to address this question by including the comparison with previous wintertime PAH concentrations which were presented in Table 2 in the original manuscript. To further address this comment, the following sentence and reference has been added to the methods: "Long sampling periods may introduce both positive and negative sampling artifacts (Ravindra et al., 2008), but the cold temperatures in Lycksele were expected to effectively limit partitioning of PAHs and organic carbon and resulting subsequent artifacts. Results from PUF and filter comparisons indicate that only phenanthrene had high concentrations in the gaseous phase."

3.] A study by Khalili et al. (AE, 29, 553, 1995) identify that 3- and 4-ring PAHs contributes major fraction (75%) of wood combustion; whereas as 5- and 6-rign up to 15%. Further, an inventory of Breivik et al. (ESP, 9, 663, 2006) and a review (AE, 42, 2895, 2008) also identify residential sector as a major source of PAHs emission in Europe. These studies follow the similar conclusions including to regulate residential wood combustion.

AR3. Although it is true that previous authors have discussed RWC as a source of PAHs, the contribution of RWC to ambient PAHs is hard to constrain with certainty due to differences in burn conditions and source material. Radiocarbon analysis provides a very accurate means of quantifying the RWC contribution to combustion products in the atmosphere. The authors agree that the novelty of this study lies in the application of compound specific radiocarbon analysis to atmospheric PAHs, not in the idea that RWC can be a significant source of atmospheric carbon. Additionally, as shown in the newly added Table 3, there is significant variability in the RWC apportionment across Europe, so regional studies are important for regional regulation. To properly acknowledge previous efforts on the subject, the authors have added the Breivik refer-

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ence and the review in the introduction in the following sentence: "Apportioning PAHs to a specific combustion source can be difficult (Hays et al., 2003;Schauer et al., 2001, 2002;McDonald et al., 2003) and inventories and reviews have been written to determine sources and review regulatory tactics (Breivik et al., 2006;Ravindra et al., 2008)."

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